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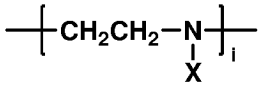
(54) PLATING SOLUTION

(57) A plating solution that enables plating with high gloss is provided. The plating solution contains a metal ion, and a PEI compound (L) having a polyethylenimine skeleton, and having a structural moiety LX represented by formula (LX), a structural moiety LY represented by formula (LY) and a structural moiety LH represented by formula (LH),

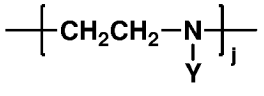
[Chem. 1]



(LX)

wherein in the formula (LX), X represents a structural moiety X1 represented by formula (X1), and i represents an integer of 1 or more,

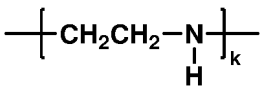
[Chem. 2]



(LY)

wherein in the formula (LY), Y represents a structural moiety Y1 represented by formula (Y1), and j represents an integer of 1 or more,

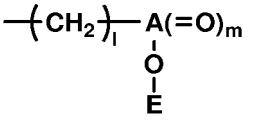
[Chem. 3]



(LH)

wherein in the formula (LH), k represents 0 or an integer of 1 or more,

[Chem. 4]



(X1)

wherein in the formula (X1), A represents C or S, E represents a monovalent metal ion, H, a methyl group, an ethyl group, or an allyl group, l represents an integer of 1 to 6, and m represents 1 or 2, and

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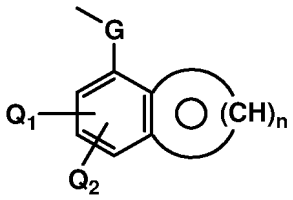
[Chem. 5]



(Y1)

wherein in the formula (Y1), G represents CH_2 or CH(OH), n represents 0 or 4, and Q_1 and Q_2 each independently represent H, an electron-withdrawing group, or an electron-donating group.

Description

TECHNICAL FIELD

[0001] The present invention relates to a plating solution. More specifically, the present invention relates to a plating solution that enables plating with high gloss.

BACKGROUND ART

[0002] Plating treatments are generally applied as one of surface treatment techniques in order to confer appearance characteristics such as decoration and functionalities such as corrosion resistance to a base material such as a resin, a metal, a glass material, or a ceramic material. Among the plating treatments, electrolytic copper plating is used as a base plating because it yields a highly ductile plating film and can prevent cracks from being caused by expansion and contraction of the material due to temperature changes. For decorative applications, smoothing of a substrate surface roughened due to etching and intrinsic unevenness of a material as well as high gloss are required.

[0003] For example, Patent Document 1 discloses an electrolytic copper plating solution containing a basic dye such as janus green B as a leveler in order to achieve a sufficiently glossy appearance. An electrolytic copper plating solution free of a basic dye as a leveler is also disclosed in, for example, Patent Document 2. Patent Document 2 discloses an electrolytic copper plating solution containing at least one aromatic reaction product of benzyl chloride and at least one polyethylenimine.

Citation List

Patent Document

[0004]

PATENT DOCUMENT 1: Japanese Unexamined Patent Application (Translation of PCT Application), Publication No. 2020-536168

Patent Document 2: Japanese Unexamined Patent Application (Translation of PCT Application), Publication No. 2020-523481

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

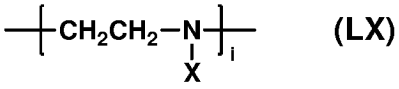
[0005] However, plating with higher gloss is desired in decorative plated products. The present invention has been made in view of the above circumstances, and an object of the present invention is to provide a plating solution that is free of a basic dye conventionally used and enables plating with higher gloss.

Means for Solving the Problems

[0006] As a result of extensive studies, the present inventors have found that a plating solution that contains a specific compound as a leveler enables the plating with high gloss, and completed the present invention.

[0007] A first aspect of the the present invention relates to a plating solution comprising: a metal ion; and a polyethylenimine (PEI) compound (L) having a polyethylenimine skeleton and having a structural moiety LX represented by the following formula (LX), a structural moiety LY represented by the following formula (LY), and a structural moiety LH represented by the following formula (LH),

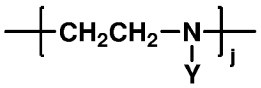
[Chem. 1]



(LX)

wherein in the formula (LX), X represents a structural moiety X1 represented by the following formula (X1), and i represents an integer of 1 or more,

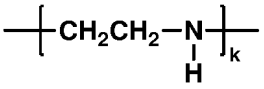
[Chem. 2]



(LY)

wherein in the formula (LY), Y represents a structural moiety Y1 represented by the following formula (Y1), and j represents an integer of 1 or more,

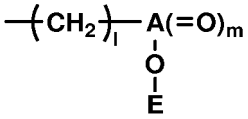
[Chem. 3]



(LH)

wherein in the formula (LH), k represents 0 or an integer of 1 or more,

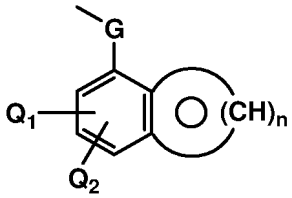
[Chem. 4]



(X1)

wherein in the formula (X1), A represents C or S, E represents a monovalent metal ion, H, a methyl group, an ethyl group, or an allyl group, l represents an integer of 1 to 6, and m represents 1 or 2, and

[Chem. 5]



(Y1)

wherein in the formula (Y1), G represents CH_2 or CH(OH), n represents 0 or 4, and Q_1 and Q_2 each independently represent H, an electron-withdrawing group, or an electron-donating group.

[0008] A second aspect of the present invention relates to the plating solution according to the first aspect, wherein a value of $\{i/(i+j+k)\}\times 100$ calculated based on i in the structural moiety LX, j in the structural moiety LY, and k in the structural moiety LH is preferably 20 to 90%.

[0009] A third aspect of the present invention relates to the plating solution according to the first or second aspect, wherein the metal ion preferably comprises a copper ion.

Effects of the Invention

[0010] According to the present invention, a plating solution that enables plating with high gloss can be provided.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0011] Hereinafter, embodiments of the present invention will be described.

Plating Solution

[0012] A plating solution according to the present invention at least contains a metal ion and a PEI compound (L). The plating solution according to the present invention may further contain an acid, a halide ion, a brightener, a surfactant, and the like.

Metal Ion

[0013] Examples of the metal ion constituting the plating solution of the present invention include, but are not limited to, ions of copper, tin, titanium, chromium, manganese, iron, nickel, cobalt, zinc, silver, gold, platinum, palladium, indium, molybdenum, tungsten, lead, rhenium, rhodium, ruthenium, osmium, iridium, bismuth, aluminum, and the like. In the plating solution according to the present invention, the metal ion preferably contains a copper ion.

[0014] The metal ion of the plating solution according to the present invention is typically obtained by dissolving a metal salt in a solvent such as water. The plating solution according to the present invention is preferably obtained by dissolving a copper-containing metal salt in water. The copper-containing metal salt is not limited to a particular copper-containing metal salt, and examples thereof include copper sulfate, copper pyrophosphate, copper acetate, etc. Among them, copper sulfate is preferable.

[0015] Copper sulfate pentahydrate is preferably used as the copper sulfate, and the content of copper sulfate pentahydrate in the plating solution according to the present invention is not limited, and is, for example, 50 to 300 g/L, and preferably 100 to 280 g/L.

Leveler

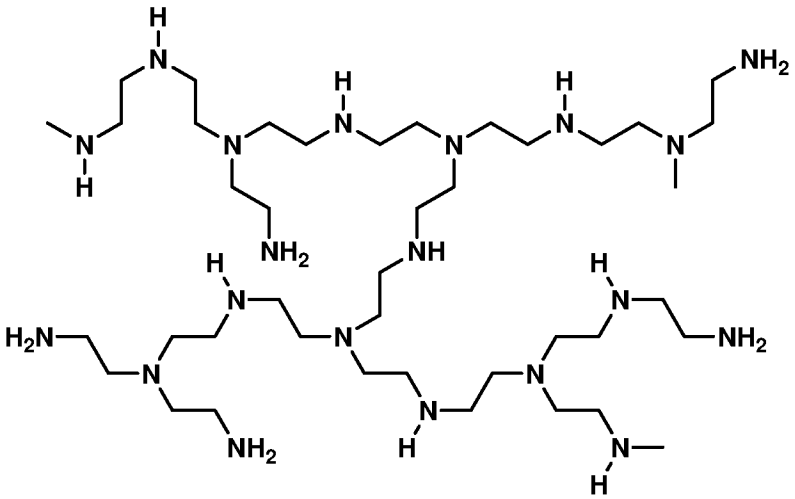
[0016] In the present invention, the PEI compound (L) is at least used as a leveler. In the present invention, one or more known levelers may be added in addition to the PEI compound (L).

PEI Compound

[0017] The PEI compound (L) has a polyethylenimine skeleton and specific structural moieties. Specifically, the PEI compound (L) has a polyethylenimine skeleton, and has a structural moiety LX represented by the following formula (LX), a structural moiety LY represented by the following formula (LY), and a structural moiety LH represented by the following formula (LH), which will be described later. The structural moiety LX, the structural moiety LY, and the structural moiety LH each have at least a skeleton of $[-(CH_2)_2-N-]$, as described later.

[0018] The polyethylenimine skeleton, as used herein, means the skeleton of polyethylenimine (PEI). The PEI compound (L) has a structure in which hydrogen atoms H bonded to the polyethylenimine skeleton are substituted with X and Y described later. The polyethylenimine skeleton is, for example, a network, branched, or linear polyethylenimine skeleton. The network polyethylenimine, as used herein, means a branched polyethylenimine in which a part or all of the branched portions of the branched polyethylenimine is bonded to another branched portion or the skeleton to form a network. An example of the network polyethylenimine is shown in the following formula (NP).

[Chem. 6]



(NP)

[0019] The polyethylenimine skeleton of the PEI compound (L) is preferably the network or branched polyethylenimine skeleton.

[0020] The PEI compound (L) is a compound in which polyethylenimine having a polyethylenimine skeleton has a number-average molecular weight of, for example, 300 to 70,000, preferably 1,100 to 10,000, and more preferably 1,100 to 1,800. The number-average molecular weight of the polyethylenimine falling within the above range is preferable, since a

metal plating film having high gloss can be easily obtained. The polyethylenimine having a polyethylenimine skeleton, as used herein, means polyethylenimine in which the atoms bonded to the polyethylenimine skeleton are only the hydrogen atoms H.

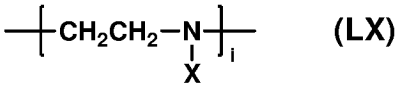
[0021] The PEI compound (L) is often obtained by reacting polyethylenimine having a polyethylenimine skeleton with a source material of X in the structural moiety LX, and a source material of Y in the structural moiety LY. In such cases, when the source material of X in the structural moiety LX, and the source material of Y in the structural moiety LY are added to the basic material polyethylenimine, the molecular weight of the PEI compound (L) is increased by an amount commensurate with the addition of the source material of X in the structural moiety LX, and the source material of Y in the structural moiety LY, without the polymerization of the basic material polyethylenimine.

[0022] In the present invention, a moiety of the PEI compound (L) in which the hydrogen atom H bonded to the polyethylenimine skeleton is substituted with X is referred to as a structural moiety LX. A moiety of the PEI compound (L) in which the hydrogen atom H bonded to the polyethylenimine skeleton is substituted with Y is referred to as a structural moiety LY. Furthermore, a moiety of the PEI compound (L) in which the hydrogen atom H bonded to the polyethylenimine skeleton is present and unsubstituted is referred to as a structural moiety LH. It should be noted that the PEI compound (L) includes at least the structural moiety LX and the structural moiety LY, and optionally includes the structural moiety LH.

Structural Moiety LX

[0023] The structural moiety LX is a structural moiety represented by the following formula (LX).

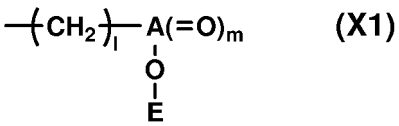
[Chem. 7]



(LX)

[0024] In the formula (LX), X represents a structural moiety X1 represented by the following formula (X1), and i represents an integer of 1 or more.

[Chem. 8]

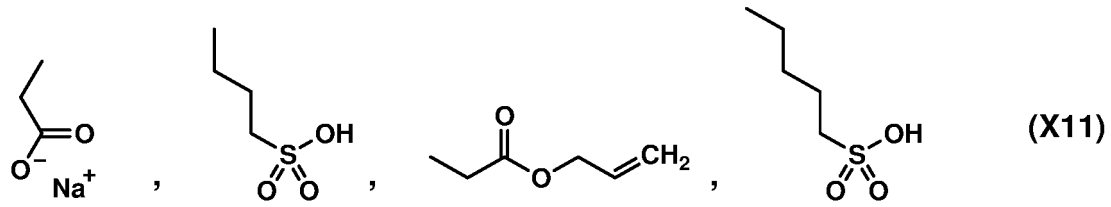


(X1)

[0025] In the formula (X1), A represents C or S, E represents a monovalent metal ion, H, a methyl group, an ethyl group, or an allyl group, l represents an integer of 1 to 6, and m represents 1 or 2. E preferably represents a monovalent metal ion, H, or an allyl group. l preferably represents an integer of 3 to 4. Examples of the monovalent metal ion include Li, Na, K, Rb, Cs, Fr, etc.

[0026] Preferred embodiments of the structural moiety represented by the structural moiety X1 include, for example, structural moieties represented by structural moieties X111, X112, X113, and X114 shown in the following formula (X11).

[Chem. 9]



(X11)

(X111) (X112) (X113) (X114)

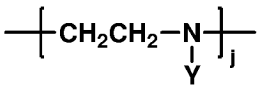
[0027] The upper end portions of the structural moieties X111, X112, and X114 correspond to the left end portion of the structural moiety X1. The left end portion of the structural moiety X113 corresponds to the left end portion of the structural

moiety X1.

Structural Moiety LY

[0028] The structural moiety LY is a structural moiety represented by the following formula (LY).

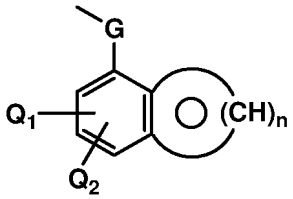
[Chem. 10]



(LY)

[0029] In the formula (LY), Y represents a structural moiety Y1 represented by the following formula (Y1), and j represents an integer of 1 or more.

[Chem. 11]



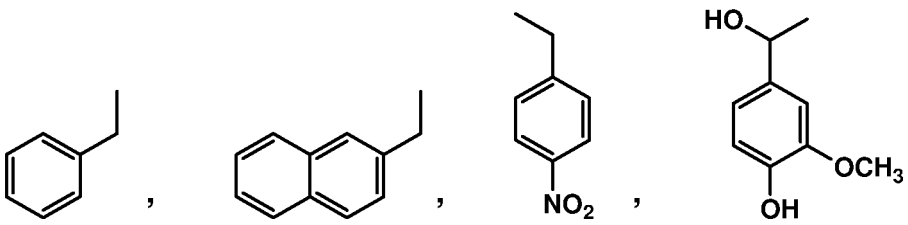
(Y1)

In the formula (Y1), G represents CH_2 or CH(OH), n represents 0 or 4, and Q_1 and Q_2 each independently represent H, an electron-withdrawing group, or an electron-donating group. When n is 0, the aryl group of the structural moiety Y1 has a structure containing one benzene ring. When n is 4, the aryl group of the structural moiety Y1 has a structure containing one naphthalene ring.

[0030] Incidentally, in the formula (Y1), Q_1 and Q_2 on the aryl group of the structural moiety Y1 each independently represent H, an electron-withdrawing group, or an electron-donating group, and are not limited to a particular group. Examples of the electron-withdrawing group include a chloro group -Cl, a fluoro group -F, a nitro group $-NO_2$, a hydroxy group -OH, etc. Examples of the electron-donating group include a methyl group $-CH_3$, a methoxy group $-OCH_3$, etc. When Q_1 and Q_2 are substituents other than the hydrogen atom H, examples of the substitution position of the substituents with respect to the portion bonded to the polyethylenimine skeleton include an ortho position, a meta position, a para position, etc.

[0031] Preferred embodiments of the structural moiety represented by the structural moiety Y1 include, for example, structural moieties represented by structural moieties Y111, Y112, Y113, and Y114 shown in the following formula (Y11).

[Chem. 12]



(Y11)

(Y111) (Y112) (Y113) (Y114)

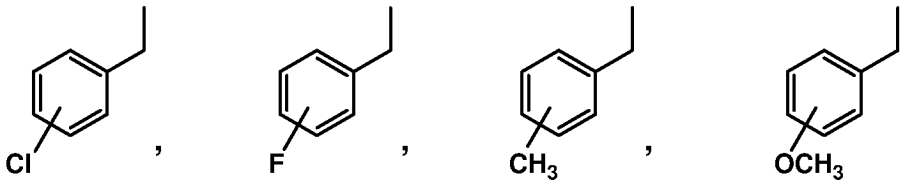
[0032] The upper end portions of the structural moieties Y111, Y112, and Y113 correspond to the upper end portion of the structural moiety Y1. The right upper end portion of the structural moiety Y114 corresponds to the upper end portion of the structural moiety Y1.

[0033] Since Q_1 and Q_2 in the formula (Y1) each independently represent H, an electron-withdrawing group, or an electron-donating group, a substituent other than the hydrogen atom H may be bonded to the aryl group in the structural moieties Y111, Y112, Y113, and Y114 shown in the formula (Y11). When Q_1 and Q_2 on the aryl group in the structural moieties Y111, Y112, Y113, and Y114 are substituents other than the hydrogen atom H, the types, numbers and positions

of the substituents are not limited, and examples of the substituents include a chloro group -Cl, a fluoro group -F, a methyl group -CH_3, and a methoxy group -OCH_3, etc.

[0034] Preferred embodiments of the structural moiety in which Q_1 and Q_2 in the formula (Y1) are substituents other than the hydrogen atom H include, for example, structural moieties shown in the following formula (Y11A).

[Chem. 13]



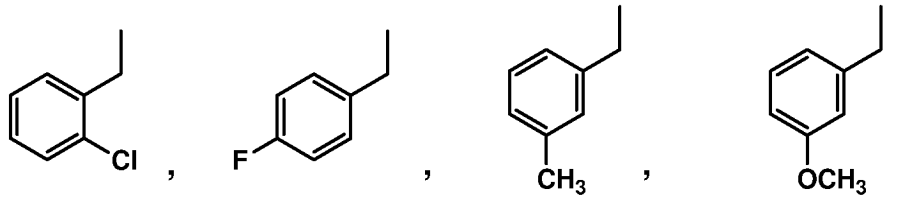
(Y11A)

(Y111-Cl) (Y111-F) (Y111-CH3) (Y111-OCH3)

[0035] The upper end portions of the structural moieties Y111-Cl, Y111-F, Y111-CH3, and Y111-OCH3 correspond to the upper end portion of the structural moiety Y1.

[0036] Particularly preferred embodiments of the structural moiety in which Q_1 and Q_2 in the formula (Y1) are substituents other than the hydrogen atom H include, for example, structural moieties shown in the following formula (Y11B).

[Chem. 14]



(Y11B)

(Y111-oCl) (Y111-pF) (Y111-mCH3) (Y111-mOCH3)

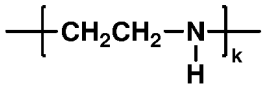
[0037] The upper end portions of the structural moieties Y111-oCl, Y111-pF, Y111-mCH3, and Y111-mOCH3 correspond to the upper end portion of the structural moiety Y1.

[0038] The structural moieties Y111-oCl (-$CH_2C_6H_4Cl$), Y111-pF (-$CH_2C_6H_4F$) , Y111-mCH3 (-$CH_2C_6H_4CH_3$), and Y111-mOCH3 (-$CH_2C_6H_4OCH_3$) each correspond to the aryl group (benzyl group) represented by the structural moiety Y111 in which one of Q_1 and Q_2 in the formula (Y1) is H and the other is Cl at the ortho position in Y111-oCl, F at the para position in Y111-pF, CH_3 at the meta position in Y111-mCH3, and OCH_3 at the meta position in Y111-mOCH3.

Structural Moiety LH

[0039] The structural moiety LH is a structural moiety represented by the following formula (LH).

[Chem. 15]



(LH)

[0040] In the formula (LH), k represents 0 or an integer of 1 or more. It should be noted that when k is 0, the PEI compound (L) is a compound containing no structural moiety LH.

[0041] In the PEI compound (L), a value of {i/(i+j+k)}×100 calculated based on i in the structural moiety LX, j in the structural moiety LY, and k in the structural moiety LH is 20 to 90%, and preferably 30 to 80%. The value of {i/(i+j+k)}×100 falling within the above range is preferable, since a metal plating film having high gloss can be easily obtained. It should be noted that the value of {i/(i+j+k)}×100 can be determined by, for example, NMR or the like.

[0042] The plating solution according to the present invention contains, for example, 0.5 to 50 mg/L, and preferably 1 to

30 mg/L of the PEI compound (L). The concentration of the PEI compound (L) in the plating solution within the above range is preferable, since a metal plating film having high gloss can be easily obtained.

Acid

[0043] The plating solution according to the present invention may contain an acid. The acid is not limited, and, for example, any desired acid among inorganic and/or organic acids may be used in accordance with the composition of the plating solution or the plating target. Examples of the inorganic acids include sulfuric acid, nitric acid, hydrohalic acids including hydrochloric acid, phosphoric acid, oxo acids including chloric acid, etc. Examples of the organic acids include alkanesulfonic acids such as methanesulfonic acid and propanesulfonic acid, alkanolsulfonic acids such as isethionic acid and propanolsulfonic acid, and aliphatic or aromatic carboxylic acids such as citric acid, tartaric acid and formic acid, etc. When a source material of the metal ion of the plating solution is copper sulfate, the plating solution preferably contains sulfuric acid as an acid.

[0044] When the acid is sulfuric acid, the content of sulfuric acid is not limited, and is, for example, 20 to 200 g/L, and preferably 30 to 150 g/L.

Halide Ion

[0045] The plating solution according to the present invention may contain a halide ion for the purpose of achieving glossy metal plating or leveling. The halide ion is not limited, and examples thereof include a chloride ion, a bromide ion, an iodide ion, etc. Among them, a chloride ion is preferable.

[0046] When the halide ion is a chloride ion, the content of the chloride ion is not limited, and is, for example, 10 to 120 mg/L, and preferably 20 to 100 mg/L.

Brightener

[0047] The plating solution according to the present invention may contain a brightener. The brightener is not limited to a particular brightener, and examples thereof include: various aldehydes such as benzaldehyde, o-chlorobenzaldehyde, 2,4,6-trichlorobenzaldehyde, m-chlorobenzaldehyde, p-nitrobenzaldehyde, p-hydroxybenzaldehyde, furfural, 1-naphthaldehyde, 2-naphthaldehyde, 2-hydroxy-1-naphthaldehyde, 3-acenaphthaldehyde, benzylideneacetone, pyridylideneacetone, furfurylideneacetone, cinnamaldehyde, anisaldehyde, salicylaldehyde, crotonaldehyde, acrolein, glutaraldehyde, paraldehyde, and vanillin; triazine, imidazole, indole, quinoline, 2-vinylpyridine, aniline, phenanthroline, neocuproine, picolinic acid, thioureas, N-(3-hydroxybutylidene) -p-sulfanilic acid, N-butylidenesulfanilic acid, N-cinnamoylidenesulfanilic acid, 2,4-diamino-6- (2'-methylimidazol-1'-yl)ethyl-1,3,5-triazine, 2,4-diamino-6-(2'-ethyl-4-methylimidazol-1'-yl)ethyl-1,3,5-triazine, 2,4-diamino-6- (2'-undecylimidazol-1'-yl)ethyl-1,3,5-triazine, phenyl salicylate; or benzothiazoles such as benzothiazole, 2-mercaptobenzothiazole, 2-methylbenzothiazole, 2-aminobenzothiazole, 2-amino-6-methoxybenzothiazole, 2-methyl-5-chlorobenzothiazole, 2-hydroxybenzothiazole, 2-amino-6-methylbenzothiazole, 2-chlorobenzothiazole, 2,5-dimethylbenzothiazole, and 5-hydroxy-2-methylbenzothiazole; and sulfides such as bis(3-sodium sulfopropyl) disulfide (SPS) and salts thereof.

[0048] The content of the brightener is not limited, and is, for example, 1 to 50 mg/L, and preferably 3 to 30 mg/L.

Surfactant

[0049] The plating solution according to the present invention may contain a surfactant. The surfactant is not limited, and examples thereof include nonionic surfactants and amphoteric surfactants, etc. The nonionic surfactants are not limited, and examples thereof include polyether compounds, etc. The polyether compounds are not limited, and examples thereof include polyalkylene glycols, polyether compounds having an alkyl group, and surfactants composed of a triblock copolymer of a hydrophilic ethylene oxide unit, a hydrophobic propylene oxide unit, and an ethylene oxide unit.

[0050] The content of the surfactant is not limited, and is, for example, 1 to 300 mg/L, and preferably 5 to 200 mg/L.

Production Method

[0051] The PEI compound (L) contained in the plating solution according to the present invention is obtained, for example, by nucleophilic addition reaction of polyethylenimine having a polyethylenimine skeleton, a source material of X in the structural moiety LX, and a source material of Y in the structural moiety LY.

[0052] The plating solution according to the present invention can be produced by any known method using the PEI compound (L) as a leveler.

Plating Method

[0053] A plating method using the plating solution according to the present invention will be described below. In this plating method, electroplating is performed on a substrate using the plating solution according to the present invention.

Substrate

[0054] The substrate is not limited, and examples thereof include substrates having a base material made of brass, copper, nickel, iron, zinc, zinc alloys, steel, resin, or the like, and having a conductive layer made of metal or the like and formed on the base material.

Temperature

[0055] For the plating solution according to the present invention, the solution temperature thereof during the electroplating is set to, for example, about 15 to 45°C, and preferably about 20 to 35°C.

Current Density

[0056] For the plating solution according to the present invention, the current density during the electroplating is set to, for example, about 0.5 to 15 A/dm^2, and preferably about 1 to 10 A/dm^2.

Plating Time

[0057] For the plating solution according to the present invention, the plating time during the electroplating is set to, for example, 5 minutes or longer, and preferably 15 minutes or longer.

[0058] According to the present invention, a plating solution that enables plating with high gloss can be obtained.

EXAMPLES

[0059] Hereinafter, the present invention will be described in more detail by way of examples, but the present invention is not limited in any way to these examples.

[Example 1]

PEI Compound

Production of Intermediate (Int. 1)

[0060] An aqueous solution of polyethylenimine (number-average molecular weight: 300) (0.90 M) was heated to 70 to 90°C, then sodium chloroacetate in an amount of 0.6 equivalents with respect to the amine value of the aqueous solution of polyethylenimine was added thereto in portions, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and a 40% by weight aqueous solution of a polyethylenimine-sodium chloroacetate adduct (Int. 1) was obtained. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.1 ppm.

Production of PEI Compound (Sample No. A1)

[0061] One hundred parts by weight of the aqueous solution of the polyethylenimine-sodium chloroacetate adduct (Int. 1) and 76 parts by weight of an aqueous sodium hydroxide solution (8.5 M) were heated to 90°C, then 20 parts by weight of benzyl chloride was added thereto in portions, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A1) was obtained. The details of the PEI compound (Sample No. A1) are shown in Table 1. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

[Table 1]

Experimental Example No.	PEI compound								Plating solution	Evaluation sample
	Sample No.	Number-average molecular weight Mn of basic material polyethylenimine	Structural moiety LX		Structural moiety LY				Sample No.	Gloss
			X		Y					
			Abbreviation of structural moiety	Structure	Abbreviation of structural moiety	Structure	Substituent(s) on aryl group in Y			
							Type	Position		
Example 1	A1	300	X111	$-CH_2COONa$	Y111	$-CH_2C_6H_5$		-	E1	704
Example 2	A2	300	X111	$-CH_2COONa$	Y111-oCl	$-CH_2C_6H_4Cl$	-Cl	ortho	E2	715
Example 3	A3	1100	X111	$-CH_2COONa$	Y111	$-CH_2C_6H_5$	-	-	E3	1126
Example 4	A4	1800	X111	$-CH_2COONa$	Y111	$-CH_2C_6H_5$	-	-	E4	1065
Example 5	A5	1800	X111	$-CH_2COONa$	Y111-pF	$-CH_2C_6H_4F$	-F	para	E5	893
Example 6	*A6*	1800	X111	$-CH_2COONa$	Y111-mCH3	$-CH_2C_6H_4CH_3$	$-CH_3$	meta	E6	1133
Example 7	A7	1800	X111	$-CH_2COONa$	Y111-mOCH3	$-CH_2C_6H_4OCH_3$	$-OCH_3$	meta	E7	967
Example 8	A8	1800	X111	$-CH_2COONa$	Y112	$-CH_2C_{10}H_7$	-	-	E8	951
Example 9	A9	1800	X111	$-CH_2COONa$	Y113	$-CH_2C_6H_4NO_2$	$-NO_2$	para	E9	654
Example 10	A10	1800	X111	$-CH_2COONa$	Y114	$-CHOHC_6H_3OCH_3OH$	$-OCH_3$/-OH	meta/para	E10	494
Example 11	A11	10000	X111	$-CH_2COONa$	Y111	$-CH_2C_6H_5$	-	-	E11	593
Example 12	A12	70000	X111	$-CH_2COONa$	Y111-oCl	$-CH_2C_6H_4Cl$	-Cl	ortho	E12	562
Example 13	A13	1800	X112	$-(CH_2)_3SO_3H$	Y111-pF	$-CH_2C_6H_4F$	-F	para	E13	490
Example 14	A14	1800	X112	$-(CH_2)_3SO_3H$	Y111-mOCH3	$-CH_2C_6H_4OCH_3$	$-OCH_3$	meta	E14	692
Example 15	A15	1800	X112	$-(CH_2)_3SO_3H$	Y113	$-CH_2C_6H_4NO_2$	$-NO_2$	para	E15	564
Example 16	A16	10000	X112	$-(CH_2)_3SO_3H$	Y111	$-CH_2C_6H_5$	-	-	E16	978

Preparation of Plating Solution

[0062] A copper plating solution (Sample No. E1) containing 220 g/L of copper sulfate pentahydrate, 70 g/L of sulfuric acid, 60 mg/L of chloride ion Cl^-, 100 mg/L of polyethylene glycol 20,000 from FUJIFILM Wako Pure Chemical Corporation as a surfactant, 8.3 mg/L of bis(3-sodium sulfopropyl) disulfide (SPS) as a brightener, and 3.0 mg/L of the PEI compound (Sample No. A1) as a leveler was prepared.

Electroplating Test

Pretreatment

[0063] First, a Hull cell brass plate was immersed at 55°C for 5 minutes using EBAPREP SK-144 (degreasing) from JCU CORPORATION, and then immersed at room temperature for 0.5 minutes using EBAVATE V-345 (acid activation) from JCU CORPORATION.

Electroplating

[0064] Cathodic electrolysis (total current: 2 A) was performed for 10 minutes at room temperature in a Hull cell test using the pretreated Hull cell brass plate and the copper plating solution (Sample No. E1). Subsequently, a rust-proofing treatment was carried out using EBAFIN G-800 from JCU CORPORATION at room temperature for 0.5 minutes to obtain an evaluation sample (Sample No. S1), which was the brass plate having a copper plating film formed on the surface thereof.

Evaluation

[0065] The evaluation sample (Sample No. S1) was set in a micro-TRI-gloss gloss meter from BYK-Gardner GmbH. A portion of the evaluation sample subjected to a current density of 3 A/dm^2 was irradiated with light at an incidence angle of 20° to measure gloss. The gloss is shown in Table 1.

[Example 2]

PEI Compound

Production of PEI Compound (Sample No. A2)

[0066] One hundred parts by weight of the aqueous solution of the polyethylenimine-sodium chloroacetate adduct (Int. 1) produced in Example 1 and 83 parts by weight of an aqueous sodium hydroxide solution (7.5 M) were heated to 90°C, then 25 parts by weight of 2-chlorobenzyl chloride was added in portions, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A2) was obtained. The details of the PEI compound (Sample No. A2) are shown in Table 1. Incidentally, the progress of the reaction was confirmed by ^1H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0067] A copper plating solution (Sample No. E2) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A2) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0068] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E2) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S2), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0069] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 1.

[Example 3]

PEI Compound

Production of Intermediate (Int. 2)

[0070] An aqueous solution of polyethylenimine (number-average molecular weight: 1,100) (0.22 M) was heated to 70 to 90°C, sodium chloroacetate in an amount of 0.6 equivalents with respect to the amine value of the aqueous solution of polyethylenimine was added in portions, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and a 32.9% by weight aqueous solution of a polyethylenimine-sodium chloroacetate adduct (Int. 2) was obtained. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.1 ppm.

Production of PEI Compound (Sample No. A3)

[0071] One hundred parts by weight of the aqueous solution of the polyethylenimine-sodium chloroacetate adduct (Int. 2) and 29 parts by weight of an aqueous sodium hydroxide solution (7.8 M) were heated to 90°C, then 6 parts by weight of benzyl chloride was added in portions, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A3) was obtained. The details of the PEI compound (Sample No. A3) are shown in Table 1. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0072] A copper plating solution (Sample No. E3) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A3) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0073] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E3) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S3), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0074] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 1.

[Example 4]

PEI Compound

Production of Intermediate (Int. 3)

[0075] An aqueous solution of polyethylenimine (number-average molecular weight: 1,800) (0.30 M) was heated to 70 to 90°C, and sodium chloroacetate (7.0 M) in an amount of 0.6 equivalents with respect to the amine value of the aqueous solution of polyethylenimine was added in portions, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and a 40% by weight aqueous solution of a polyethylenimine-sodium chloroacetate adduct (Int. 3) was obtained. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.1 ppm.

Production of PEI Compound (Sample No. A4)

[0076] One hundred parts by weight of the aqueous solution of the polyethylenimine-sodium chloroacetate adduct (Int. 3) and 90 parts by weight of an aqueous sodium hydroxide solution (6.6 M) were heated to 90°C, then 70 parts by weight of benzyl chloride was added in portions, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A4) was obtained. The details of the PEI compound (Sample No. A4) are shown in Table 1. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0077] A copper plating solution (Sample No. E4) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A4) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0078] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E4) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S4), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0079] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 1.

[Example 5]

PEI Compound

Production of PEI Compound (Sample No. A5)

[0080] One hundred parts by weight of the aqueous solution of the polyethylenimine-sodium chloroacetate adduct (Int. 3) produced in Example 4 and 68 parts by weight of an aqueous sodium hydroxide solution (9.6 M) were heated to 90°C, then 23 parts by weight of 4-fluorobenzyl chloride was added in portions, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A5) was obtained. The details of the PEI compound (Sample No. A5) are shown in Table 1. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0081] A copper plating solution (Sample No. E5) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A5) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0082] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E5) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S5), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0083] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 1.

[Example 6]

PEI Compound

Production of PEI Compound (Sample No. A6)

[0084] One hundred parts by weight of the aqueous solution of the polyethylenimine-sodium chloroacetate adduct (Int. 3) produced in Example 4 and 68 parts by weight of an aqueous sodium hydroxide solution (9.6 M) were heated to 90°C, then 22 parts by weight of 3-methylbenzyl chloride was added in portions, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A6) was obtained. The details of the PEI compound (Sample No. A6) are shown in Table 1. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0085] A copper plating solution (Sample No. E6) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A6) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0086] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E6) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S6), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0087] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 1.

[Example 7]

PEI Compound

Production of PEI Compound (Sample No. A7)

[0088] One hundred parts by weight of the aqueous solution of the polyethylenimine-sodium chloroacetate adduct (Int. 3) produced in Example 4 and 69 parts by weight of an aqueous sodium hydroxide solution (9.6 M) were heated to 90°C, then 25 parts by weight of 3-methoxybenzyl chloride was added in portions, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A7) was obtained. The details of the PEI compound (Sample No. A7) are shown in Table 1. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0089] A copper plating solution (Sample No. E7) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A7) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0090] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E7) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S7), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0091] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 1.

[Example 8]

PEI Compound

Production of PEI Compound (Sample No. A8)

[0092] One hundred parts by weight of the aqueous solution of the polyethylenimine-sodium chloroacetate adduct (Int. 3) produced in Example 4 and 54 parts by weight of an aqueous sodium hydroxide solution (13.3 M) were heated to 90°C, then 28 parts by weight of 2-(chloromethyl)naphthalene were added, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and 168 parts by weight of pure water was added thereto to obtain an aqueous solution of a PEI compound (Sample No. A8). The details of the PEI compound (Sample No. A8) are shown in Table 1. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0093] A copper plating solution (Sample No. E8) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A8) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0094] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E8) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S8), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0095] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 1.

[Example 9]

PEI Compound

Production of PEI Compound (Sample No. A9)

[0096] One hundred parts by weight of the aqueous solution of the polyethylenimine-sodium chloroacetate adduct (Int. 3) produced in Example 4 and 75 parts by weight of an aqueous sodium hydroxide solution (8.4 M) were heated to 90°C, then 27 parts by weight of 4-nitrobenzyl chloride was added, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and 169 parts by weight of pure water was added to obtain an aqueous solution of a PEI compound (Sample No. A9). The details of the PEI compound (Sample No. A9) are shown in Table 1. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0097] A copper plating solution (Sample No. E9) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A9) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0098] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E9) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S9), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0099] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 1.

[Example 10]

PEI Compound

Production of PEI Compound (Sample No. A10)

[0100] One hundred parts by weight of the aqueous solution of the polyethylenimine-sodium chloroacetate adduct (Int. 3) produced in Example 4 and 5 parts by weight of vanillin were heated to 80 to 90°C, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A10) was obtained. The details of the PEI compound (Sample No. A10) are shown in Table 1. Incidentally, the progress of the reaction was confirmed by ^{13}C NMR based on the disappearance of a signal around 191 ppm.

Preparation of Plating Solution

[0101] A copper plating solution (Sample No. E10) was prepared in the same manner as in Example 1 except that the

PEI compound (Sample No. A10) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0102] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E10) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S10), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0103] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 1.

[Example 11]

PEI Compound

Production of Intermediate (Int. 4)

[0104] An aqueous solution of polyethylenimine (number-average molecular weight: 10,000) (0.017 M) was heated to 70 to 90°C, then sodium chloroacetate in an amount of 0.6 equivalents with respect to the amine value of the aqueous solution of polyethylenimine was added in portions, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and a 40% by weight aqueous solution of a polyethylenimine-sodium chloroacetate adduct (Int. 4) was obtained. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.1 ppm.

Production of PEI Compound (Sample No. A11)

[0105] One hundred parts by weight of the aqueous solution of the polyethylenimine-sodium chloroacetate adduct (Int. 4) and 66 parts by weight of an aqueous sodium hydroxide solution (10.2 M) were heated to 90°C, then 20 parts by weight of benzyl chloride was added in portions, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A11) was obtained. The details of the PEI compound (Sample No. A11) are shown in Table 1. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0106] A copper plating solution (Sample No. E11) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A11) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0107] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E11) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S11), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0108] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 1.

[Example 12]

PEI Compound

Production of Intermediate (Int. 5)

[0109] An aqueous solution of polyethylenimine (number-average molecular weight: 70,000) (0.004 M) was heated to 70 to 90°C, then sodium chloroacetate in an amount of 0.6 equivalents with respect to the amine value of the aqueous solution of polyethylenimine was added in portions, and the reaction was allowed to proceed for 2 hours. The mixture was

cooled to room temperature, and a 17% by weight aqueous solution of a polyethylenimine-sodium chloroacetate adduct (Int. 5) was obtained. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.1 ppm.

Production of PEI Compound (Sample No. A12)

[0110] One hundred parts by weight of the aqueous solution of the polyethylenimine-sodium chloroacetate adduct (Int. 5) and 130 parts by weight of an aqueous sodium hydroxide solution (2.8 M) were heated to 90°C, then 5 parts by weight of 2-chlorobenzyl chloride was added in portions, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A12) was obtained. The details of the PEI compound (Sample No. A12) are shown in Table 1. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0111] A copper plating solution (Sample No. E12) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A12) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0112] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E12) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S12), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0113] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 1.

[Example 13]

PEI Compound

Production of Intermediate (Int. 6)

[0114] An aqueous solution of polyethylenimine (number-average molecular weight: 1,800) (0.17 M) was heated to 70 to 90°C, and 1,3-propanesultone in an amount of 0.3 equivalents with respect to the amine value of the aqueous solution of polyethylenimine was reacted therewith for 2 hours. The mixture was cooled to room temperature, and a 34% by mass aqueous solution of a polyethylenimine-1,3-propanesultone adduct (Int. 6) was obtained. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.49 ppm.

Production of PEI Compound (Sample No. A13)

[0115] One hundred parts by weight of the aqueous solution of the polyethylenimine-1,3-propanesultone adduct (Int. 6), 150 parts by weight of pure water, then 20 parts by weight of 4-fluorobenzyl chloride were heated to 90°C, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A13) was obtained. The details of the PEI compound (Sample No. A13) are shown in Table 1. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0116] A copper plating solution (Sample No. E13) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A13) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0117] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E13) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No.

S13), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0118] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 1.

[Example 14]

PEI Compound

Production of PEI Compound (Sample No. A14)

[0119] One hundred parts by weight of the aqueous solution of the polyethylenimine-1,3-propanesultone adduct (Int. 6) produced in Example 13, 150 parts by weight of pure water, and 22 parts by weight of 3-methoxybenzyl chloride were heated to 90°C, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A14) was obtained. The details of the PEI compound (Sample No. A14) are shown in Table 1. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0120] A copper plating solution (Sample No. E14) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A14) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0121] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E14) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S14), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0122] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 1.

[Example 15]

PEI Compound

Production of PEI Compound (Sample No. A15)

[0123] One hundred parts by weight of the aqueous solution of the polyethylenimine-1,3-propanesultone adduct (Int. 6) produced in Example 13, 200 parts by weight of pure water, and 23 parts by weight of 4-nitrobenzyl chloride were heated to 90°C, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A15) was obtained. The details of the PEI compound (Sample No. A15) are shown in Table 1. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0124] A copper plating solution (Sample No. E15) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A15) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0125] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E15) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S15), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0126] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 1.

[Example 16]

PEI Compound

Production of Intermediate (Int. 7)

[0127] An aqueous solution of polyethylenimine (number-average molecular weight: 10,000) (0.015 M) was heated to 70 to 90°C, and 1,3-propanesultone in an amount of 0.3 equivalents with respect to the amine value of the aqueous solution of polyethylenimine was reacted therewith for 2 hours. The mixture was cooled to room temperature, and a 23% by weight aqueous solution of a polyethylenimine-1,3-propanesultone adduct (Int. 7) was obtained. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.49 ppm.

Production of PEI Compound (Sample No. A16)

[0128] One hundred parts by weight of the aqueous solution of the polyethylenimine-1,3-propanesultone adduct (Int. 7) and 6 parts by weight of benzyl chloride were heated to 80 to 90°C, and the reaction was allowed to proceed for 3 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A16) was obtained. The details of the PEI compound (Sample No. A16) are shown in Table 1. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0129] A copper plating solution (Sample No. E16) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A16) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0130] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E16) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S16), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0131] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 1.

[Example 17]

PEI Compound

Production of Intermediate (Int. 8)

[0132] An aqueous solution of polyethylenimine (number-average molecular weight: 1,100) (0.12 M) was heated to 70 to 90°C, and allyl chloroacetate in an amount of 0.2 equivalents with respect to the amine value of the aqueous solution of polyethylenimine was reacted therewith for 2 hours. The mixture was cooled to room temperature, and a 17% by weight aqueous solution of a polyethylenimine-allyl chloroacetate adduct (Int. 8) was obtained. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.1 ppm.

Production of PEI Compound (Sample No. A17)

[0133] One hundred parts by weight of the aqueous solution of the polyethylenimine-allyl chloroacetate adduct (Int. 8) and 23 parts by weight of aqueous sodium hydroxide solution (1.9 M) were heated to 90°C, then 6 parts by weight of benzyl chloride was added in portions, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A17) was obtained. The details of the PEI compound (Sample No. A17) are shown in Table 2. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR

based on the disappearance of a signal around 4.5 ppm.

[Table 2]

Experimental Example No.	PEI compound								Plating solution	Evaluation sample
	Sample No.	Number-average molecular weight Mn of basic material polyethylenimine	Structural moiety LX		Structural moiety LY				Sample No.	Gloss
			X		Y					
			Abbreviation of structural moiety	Structure	Abbreviation of structural moiety	Structure	Substituent(s) on aryl group in Y			
							Type	Position		
Example 17	A17	1100	X113	$-CH_2COOCH_2CH=CH_2$	Y111	$-CH_2C_6H_5$	-	-	E17	595
Example 18	A18	1800	X113	$-CH_2COOCH_2CH=CH_2$	Y111	$-CH_2C_6H_5$	-	-	E18	1126
Example 19	A19	1800	X113	$-CH_2COOCH_2CH=CH_2$	Y111-oCl	$-CH_2C_6H_4Cl$	-Cl	ortho	E19	610
Example 20	A20	1800	X113	$-CH_2COOCH_2CH=CH_2$	Y111-pF	$-CH_2C_6H_4F$	-F	para	E20	645
Example 21	A21	1800	X113	$-CH_2COOCH_2CH=CH_2$	Y111-mCH3	$-CH_2C_6H_4CH_3$	$-CH_3$	meta	E21	528
Example 22	A22	1800	X113	$-CH_2COOCH_2CH=CH_2$	Y111-mOCH3	$-CH_2C_6H_4OCH_3$	$-OCH_3$	meta	E22	864
Example 23	A23	1800	X113	$-CH_2COOCH_2CH=CH_2$	Y113	$-CH_2C_6H_4NO_2$	$-NO_2$	para	E23	536
Example 24	A24	10000	X113	$-CH_2COOCH_2CH=CH_2$	Y111	$-CH_2C_6H_5$	-	-	E24	756
Example 25	A25	1800	X114	$-(CH_2)_4SO_3H$	Y111	$-CH_2C_6H_5$	-	-	E25	526
Example 26	A4	1800	X111	$-CH_2COONa$	Y111	$-CH_2C_6H_5$	-	-	E26	1249
Example 27	A4	1800	X111	$-CH_2COONa$	Y111	$-CH_2C_6H_5$	-	-	E27	1215
Comparative Example 1	-	-	-	-	-	-	-	-	E28	468
Comparative Example 2	-	-	-	-	-	-	-	-	E29	389

Preparation of Plating Solution

[0134] A copper plating solution (Sample No. E17) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A17) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0135] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E17) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S17), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0136] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 2.

[Example 18]

PEI Compound

Production of Intermediate (Int. 9)

[0137] An aqueous solution of polyethylenimine (number-average molecular weight: 1,800) (0.10 M) was heated to 70 to 90°C, and allyl chloroacetate in an amount of 0.4 equivalents with respect to the amine value of the aqueous solution of polyethylenimine was reacted therewith for 2 hours. The mixture was cooled to room temperature, and a 19% by weight aqueous solution of a polyethylenimine-allyl chloroacetate adduct (Int. 9) was obtained. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.1 ppm.

Production of PEI Compound (Sample No. A18)

[0138] One hundred parts by weight of the aqueous solution of the polyethylenimine-allyl chloroacetate adduct (Int. 9) and 19 parts by weight of an aqueous sodium hydroxide solution (4.4 M) were heated to 90°C, then 5 parts by weight of benzyl chloride was added in portions, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and 107 parts by weight of pure water was added to obtain an aqueous solution of a PEI compound (Sample No. A18). The details of the PEI compound (Sample No. A18) are shown in Table 2. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0139] A copper plating solution (Sample No. E18) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A18) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0140] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E18) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S18), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0141] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 2.

[Example 19]

PEI Compound

Production of Intermediate (Int. 10)

[0142] An aqueous solution of polyethylenimine (number-average molecular weight: 1,800) (0.10 M) was heated to 70 to

90°C, and allyl chloroacetate in an amount of 0.2 equivalents with respect to the amine value of the aqueous solution of polyethylenimine was reacted therewith for 2 hours. The mixture was cooled to room temperature, and a 15% by weight aqueous solution of a polyethylenimine-allyl chloroacetate adduct (Int. 10) was obtained. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.1 ppm.

Production of PEI Compound (Sample No. A19)

[0143] One hundred parts by weight of the aqueous solution of the polyethylenimine-allyl chloroacetate adduct (Int. 10) and 80 parts by weight of an aqueous sodium hydroxide solution (0.8 M) were heated to 90°C, then 10 parts by weight of 2-chlorobenzyl chloride was added in portions, and the reaction was allowed to proceed for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A19) was obtained. The details of the PEI compound (Sample No. A19) are shown in Table 2. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0144] A copper plating solution (Sample No. E19) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A19) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0145] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E19) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S19), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0146] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 2.

[Example 20]

PEI Compound

Production of PEI Compound (Sample No. A20)

[0147] One hundred parts by weight of the aqueous solution of the polyethylenimine-allyl chloroacetate adduct (Int. 10) produced in Example 19 and 76 parts by weight of an aqueous sodium hydroxide solution (1.7 M) were heated to 90°C, and 9 parts by weight of 4-fluorobenzyl chloride was reacted therewith for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A20) was obtained. The details of the PEI compound (Sample No. A20) are shown in Table 2. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0148] A copper plating solution (Sample No. E20) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A20) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0149] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E20) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S20), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0150] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 2.

[Example 21]

PEI Compound

Production of PEI Compound (Sample No. A21)

[0151] One hundred parts by weight of the aqueous solution of the polyethylenimine-allyl chloroacetate adduct (Int. 10) produced in Example 19 and 86 parts by weight of an aqueous sodium hydroxide solution (1.4 M) were heated to 90°C, and 8 parts by weight of 3-methylbenzyl chloride was reacted therewith for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A21) was obtained. The details of the PEI compound (Sample No. A21) are shown in Table 2. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0152] A copper plating solution (Sample No. E21) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A21) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0153] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E21) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S21), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0154] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 2.

[Example 22]

PEI Compound

Production of PEI Compound (Sample No. A22)

[0155] One hundred parts by weight of the aqueous solution of the polyethylenimine-allyl chloroacetate adduct (Int. 10) produced in Example 19 and 63 parts by weight of an aqueous sodium hydroxide solution (2 M) were heated to 90°C, and 10 parts by weight of 3-methoxybenzyl chloride was reacted therewith for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A22) was obtained. The details of the PEI compound (Sample No. A22) are shown in Table 2. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0156] A copper plating solution (Sample No. E22) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A22) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0157] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E22) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S22), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0158] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 2.

[Example 23]

PEI Compound

Production of PEI Compound (Sample No. A23)

[0159] One hundred parts by weight of the aqueous solution of the polyethylenimine-allyl chloroacetate adduct (Int. 10) produced in Example 19 and 42 parts by weight of an aqueous sodium hydroxide solution (1.5 M) were heated to 90°C, and 10 parts by weight of 4-nitrobenzyl chloride was reacted therewith for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A23) was obtained. The details of the PEI compound (Sample No. A23) are shown in Table 2. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0160] A copper plating solution (Sample No. E23) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A23) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0161] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E23) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S23), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0162] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 2.

[Example 24]

PEI Compound

Production of Intermediate (Int. 11)

[0163] An aqueous solution of polyethylenimine (number-average molecular weight: 10,000) (0.11 M) was heated to 70 to 90°C, then allyl chloroacetate in an amount of 0.2 equivalents with respect to the amine value of the aqueous solution of polyethylenimine was reacted with therewith for 2 hours. The mixture was cooled to room temperature, and a 12% by weight aqueous solution of a polyethylenimine-allyl chloroacetate adduct (Int. 11) was obtained. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.1 ppm.

Production of PEI Compound (Sample No. A24)

[0164] One hundred parts by weight of the aqueous solution of the polyethylenimine-allyl chloroacetate adduct (Int. 11) was heated to 90°C, and 5 parts by weight of benzyl chloride was reacted therewith for 2 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A24) was obtained. The details of the PEI compound (Sample No. A24) are shown in Table 2. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0165] A copper plating solution (Sample No. E24) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A24) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0166] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E24) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S24), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0167] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 2.

[Example 25]

PEI Compound

Production of Intermediate (Int. 12)

[0168] An aqueous solution of polyethylenimine (number-average molecular weight: 1,800) (0.13 M) was heated to 70 to 90°C, and 1,4-butanesultone in an amount of 0.6 equivalents with respect to the amine value of the aqueous solution of polyethylenimine was reacted therewith for 2 hours. The mixture was cooled to room temperature, and a 38% by weight aqueous solution of a polyethylenimine-1,4-butanesultone adduct (Int. 12) was obtained. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.49 ppm.

Production of PEI Compound (Sample No. A25)

[0169] One hundred parts by weight of the aqueous solution of the polyethylenimine-1,4-butanesultone adduct (Int. 12) and 7 parts by weight of benzyl chloride were heated to 80 to 90°C, and the reaction was allowed to proceed for 3 hours. The mixture was cooled to room temperature, and an aqueous solution of a PEI compound (Sample No. A25) was obtained. The details of the PEI compound (Sample No. A25) are shown in Table 2. Incidentally, the progress of the reaction was confirmed by ^{1}H NMR based on the disappearance of a signal around 4.5 ppm.

Preparation of Plating Solution

[0170] A copper plating solution (Sample No. E25) was prepared in the same manner as in Example 1 except that the PEI compound (Sample No. A25) was used instead of the PEI compound (Sample No. A1).

Electroplating Test

[0171] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E25) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S25), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0172] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 2.

[Example 26]

Preparation of Plating Solution

[0173] A copper plating solution (Sample No. E26) was prepared in the same manner as in Example 1 except that polyethylene glycol 4,000 from FUJIFILM Wako Pure Chemical Corporation was used instead of the polyethylene glycol 20,000 from FUJIFILM Wako Pure Chemical Corporation. The copper plating solution (Sample No. E26) is identical to the copper plating solution (Sample No. E4) prepared in Example 4 except that only the surfactant therein is modified.

Electroplating Test

[0174] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E26) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S26), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0175] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 2.

[Example 27]

Preparation of Plating Solution

[0176] A copper plating solution (Sample No. E27) was prepared in the same manner as in Example 1 except that a nonionic surfactant ADEKA Pluronic (registered) L-64 from ADEKA CORPORATION was used instead of the polyethylene glycol 20,000 from FUJIFILM Wako Pure Chemical Corporation. The copper plating solution (Sample No. E27) is identical to the copper plating solution (Sample No. E4) prepared in Example 4 except that only the surfactant therein is modified.

Electroplating Test

[0177] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E27) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S27), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0178] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 2.

[Comparative Example 1]

Preparation of Plating Solution

[0179] A copper plating solution (Sample No. E28) containing 220 g/L of copper sulfate pentahydrate, 70 g/L of sulfuric acid, 60 mg/L of chloride ion Cl^-, 100 mg/L of polyethylene glycol 20,000 from FUJIFILM Wako Pure Chemical Corporation as a surfactant, 8.3 mg/L of bis(3-sodium sulfopropyl) disulfide (SPS) as a brightener, and 3.0 mg/L of janus green B as a leveler was prepared.

Electroplating Test

[0180] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E28) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S28), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0181] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 2.

[Comparative Example 2]

Preparation of Plating Solution

[0182] A copper plating solution (Sample No. E29) containing 220 g/L of copper sulfate pentahydrate, 70 g/L of sulfuric acid, 60 mg/L of chloride ion Cl^-, 100 mg/L of polyethylene glycol 20,000 from FUJIFILM Wako Pure Chemical Corporation as a surfactant, 8.3 mg/L of bis(3-sodium sulfopropyl) disulfide (SPS) as a brightener, and 3.0 mg/L of an aromatic reaction product of benzyl chloride and polyalkylenimine as a leveler was prepared.

Electroplating Test

[0183] Cathodic electrolysis was performed in the same manner as in Example 1 except that the copper plating solution (Sample No. E29) was used instead of the copper plating solution (Sample No. E1), and an evaluation sample (Sample No. S29), which was a brass plate having a copper plating film formed on the surface thereof, was obtained.

Evaluation

[0184] The gloss was measured in the same manner as in Example 1. The gloss is shown in Table 2.

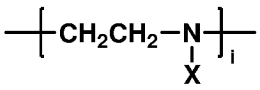
[0185] It can be seen from Tables 1 and 2 that the evaluation samples prepared in Examples (samples Nos. E1 to E27) have higher gloss than Comparative Examples (samples Nos. E28 and E29).

Claims

1. A plating solution comprising:

a metal ion; and
a PEI compound (L) having a polyethylenimine skeleton and having a structural moiety LX represented by formula (LX), a structural moiety LY represented by formula (LY) and a structural moiety LH represented by formula (LH),

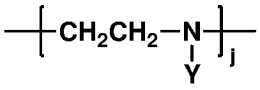
[Chem. 1]



(LX)

wherein in the formula (LX), X represents a structural moiety X1 represented by formula (X1), and i represents an integer of 1 or more,

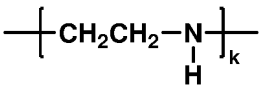
[Chem. 2]



(LY)

wherein in the formula (LY), Y represents a structural moiety Y1 represented by formula (Y1), and j represents an integer of 1 or more,

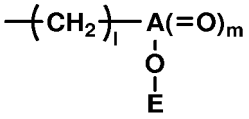
[Chem. 3]



(LH)

wherein in the formula (LH), k represents 0 or an integer of 1 or more,

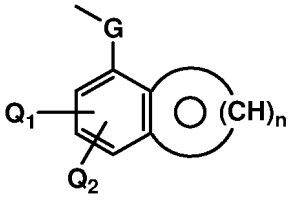
[Chem. 4]



(X1)

wherein in the formula (X1), A represents C or S, E represents a monovalent metal ion, H, a methyl group, an ethyl group, or an allyl group, l represents an integer of 1 to 6, and m represents 1 or 2, and

[Chem. 5]



(Y1)

wherein in the formula (Y1), G represents CH_2 or CH(OH), n represents 0 or 4, and Q_1 and Q_2 each independently represent H, an electron-withdrawing group, or an electron-donating group.

2. The plating solution according to claim 1, wherein a value of {i/(i+j+k)}×100 calculated based on i in the structural moiety LX, j in the structural moiety LY, and k in the structural moiety LH is 20 to 90%.

3. The plating solution according to claim 1 or 2, wherein the metal ion comprises a copper ion.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/023544

A. CLASSIFICATION OF SUBJECT MATTER

C25D 3/38(2006.01)i
FI: C25D3/38 101

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)

C25D3/38

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 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

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 2001-279228 A (AJINOMOTO CO., INC.) 10 October 2001 (2001-10-10) entire text	1-3
A	JP 2004-043957 A (ENTHONE INC.) 12 February 2004 (2004-02-12) entire text, all drawings	1-3
A	CN 110117801 A (ZHENGZHOU ZHITAO INFORMATION TECHNOLOGY CO., LTD.) 13 August 2019 (2019-08-13) entire text	1-3
A	JP 2005-536579 A (BASF AKTIENGESELLSCHAFT) 02 December 2005 (2005-12-02) entire text	1-3

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

* Special categories of cited documents:
"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
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"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
"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
"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
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 August 2023	**12 September 2023**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/023544

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2001-279228 A	10 October 2001	(Family: none)	
JP 2004-043957 A	12 February 2004	US 2003/0168343 A1 entire text WO 2005/066391 A1 EP 1697561 A1 DE 10309085 A CN 1444258 A TW 200304966 A KR 10-2006-0127067 A	
CN 110117801 A	13 August 2019	(Family: none)	
JP 2005-536579 A	02 December 2005	US 2005/0209117 A1 entire text WO 2004/001099 A2 EP 1525247 A2 DE 10227362 A CA 2489916 A AU 2003246562 A	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2020536168 W **[0004]**
- JP 2020523481 W **[0004]**