(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 896 720 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
22.07.2015 Bulletin 2015/30

(21) Application number: **13837102.6**

(22) Date of filing: **12.09.2013**

(51) Int Cl.:
C23C 18/30 $^{(2006.01)}$

(86) International application number:
PCT/JP2013/074714

(87) International publication number:
WO 2014/042215 (20.03.2014 Gazette 2014/12)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(30) Priority: **13.09.2012 JP 2012201584**
11.01.2013 JP 2013003605
15.03.2013 JP 2013053574

(71) Applicant: **Nissan Chemical Industries, Ltd.**
Chiyoda-ku
Tokyo 101-0054 (JP)

(72) Inventors:
- **SAITO, Daigo**
  Funabashi-shi
  Chiba 274-8507 (JP)
- **KOJIMA, Keisuke**
  Funabashi-shi
  Chiba 274-8507 (JP)

(74) Representative: **Hoffmann Eitle**
Patent- und Rechtsanwälte PartmbB
Arabellastraße 30
81925 München (DE)

(54) ELECTROLESS PLATING BASE AGENT

(57) It is an object of the present invention to provide a novel primer for use in pretreatment steps in electroless plating which is environmentally friendly, by which process is easy with fewer steps, and which can realize cost reduction. A primer for forming a metal plating film on a base material by electroless plating, the primer comprising: a hyperbranched polymer having an ammonium group at a molecular terminal and a weight-average molecular weight of 500 to 5,000,000; a metal fine particle; and an alkoxysilane.

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The present invention relates to a primer for electroless plating comprising a hyperbranched polymer, metal fine particles, and an alkoxysilane.

BACKGROUND ART

[0002] Electroless plating is extensively employed in various fields including decorating applications where a luxurious and aesthetic appearance is imparted to a resin molded body for an automotive part and the like, electromagnetic shielding, and wiring technology for a printed circuit board, a large scale integrated circuit, and the like. The reason is that electroless plating can produce a coating film with a uniform thickness regardless of the kind and shape of the base material only by immersing the base material in a plating solution and can produce a metal plating film also on a nonconductor such as plastic, ceramic, and glass.

[0003] Generally, when a metal plating film is formed on a base material (an object to be plated) by electroless plating, a pretreatment for electroless plating to increase adhesion between the base material and the metal plating film is carried out. Specifically, the surface to be treated is roughened and/or hydrophilized by various etching means, followed by sensitization where an adsorbing substance that promotes adsorption of a plating catalyst on the surface to be treated is provided on the surface to be treated and activation where the plating catalyst is allowed to adsorb on the surface to be treated. Typically, sensitization involves immersion of the object to be treated in an acidic solution of stannous chloride to allow the metal (Sn^{2+}) capable of acting as a reducing agent to deposit on the surface to be treated. The sensitized surface to be treated is immersed in an acidic solution of palladium chloride for activation. In this step, the palladium ion in the solution is reduced by the metal that is a reducing agent (tin ion: Sn^{2+}) and deposited on the surface to be treated as an active palladium catalyst nucleus. After this pretreatment, the base material is immersed in an electroless plating solution to form a metal plating film on the surface to be treated.

[0004] On the other hand, hyperbranched polymers classified as dendritic polymers have intentionally introduced branches, the most prominent feature of which is a large number of terminal groups. If reactive functional groups are added to the terminal groups, the polymer has reactive functional groups quite densely and is expected to be applied as, for example, a highly sensitive scavenger for functional substances such as catalysts, a sensitive multifunctional cross-linking agent, or a dispersing or coating agent for metals or metal oxides.

[0005] For example, an example has been described where a composition containing a hyperbranched polymer having an ammonium group and metal fine particles is used as a reduction catalyst (Patent Document 1).

SUMMARY OF THE INVENTION

Problem to be Solved by the Invention

[0006] As described above, the conventional electroless plating process needs some improvements in terms of the environmental impact, the costs, and the troublesome operation, including the use of a chromium compound (chromic acid) in the roughening step carried out in the pretreatment and the many steps involved in the pretreatment.

[0007] As the technology for molding a resin housing has recently improved, a method of plating the surface of a finely produced housing as-is is required. In particular, due to fine electronic circuit formation and faster transmission of electric signals, a method of performing electroless plating that provides a highly adhesive plating film on a smooth substrate is required.

[0008] The present invention focuses on these problems and aims to provide a novel, environmentally friendly primer for use in the pretreatment steps in electroless plating, by which process is easy with fewer steps and which can realize cost reduction.

Means for Solving the Problems

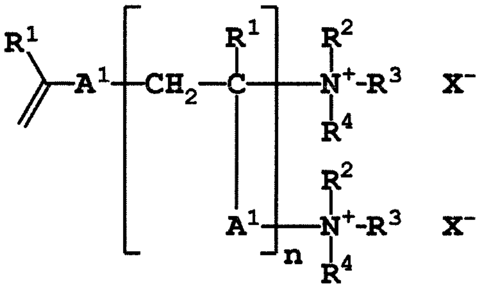
[0009] As a result of intensive study to achieve the objects, the inventors of the present invention have found that a layer obtained by combining a hyperbranched polymer having an ammonium group at a molecular terminal, metal fine particles, and an alkoxysilane and coating a base material with the combination has excellent platability and adhesion as a priming layer for electroless metal plating and completed the present invention.

[0010] Specifically, according to a first aspect, the present invention relates to a primer for forming a metal plating film on a base material by electroless plating, the primer comprising: (a) a hyperbranched polymer having an ammonium group at a molecular terminal and a weight-average molecular weight of 500 to 5,000,000; (b) a metal fine particle; and

(c) an alkoxysilane having an amino group optionally substituted with an aliphatic group, or an epoxy group, or an oligomer of the alkoxysilane.

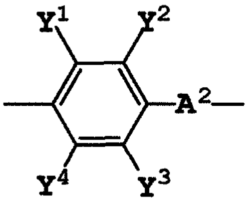
[0011] According to a second aspect, the present invention relates to the primer according to the first aspect, in which the ammonium group of the hyperbranched polymer (a) is attached to the metal fine particle (b) to form a complex.

[0012] According to a third aspect, the present invention relates to the primer according to the first aspect or the second aspect, in which the hyperbranched polymer (a) is a hyperbranched polymer of Formula [1]:



[1]

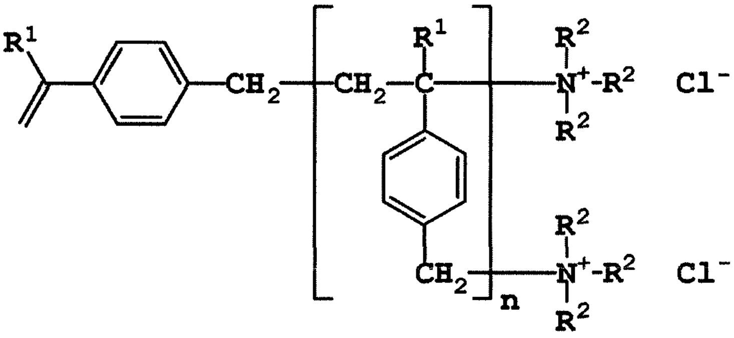
(where R^1s are each independently a hydrogen atom or a methyl group; R^2 to R^4 are each independently a hydrogen atom, a linear, branched, or cyclic alkyl group having a carbon atom number of 1 to 20, a C_{7-20} arylalkyl group, or $-(CH_2CH_2O)_mR^5$ (where R^5 is a hydrogen atom or a methyl group; and m is an integer of 2 to 100) (where the alkyl group and the arylalkyl group are optionally substituted with an alkoxy group, a hydroxy group, an ammonium group, a carboxy group, or a cyano group), or two groups of R^2 to R^4 together represent a linear, branched, or cyclic alkylene group, or R^2 to R^4 together with a nitrogen atom to which R^2 to R^4 are bonded optionally form a ring; X^- is an anion; n is the number of repeating unit structures and an integer of 5 to 100,000; and A^1 is a structure of Formula [2]:



[2]

(where A^2 is a linear, branched, or cyclic alkylene group having a carbon atom number of 1 to 30 optionally containing an ether bond or an ester bond; and Y^1 to Y^4 are each independently a hydrogen atom, a C_{1-20} alkyl group, a C_{1-20} alkoxy group, a nitro group, a hydroxy group, an amino group, a carboxy group, or a cyano group)).

[0013] According to a fourth aspect, the present invention relates to the primer according to the third aspect, in which the hyperbranched polymer (a) is a hyperbranched polymer of Formula [3]:



[3]

(where R^1, R^2, and n have the same meanings as described above).

[0014] According to a fifth aspect, the present invention relates to the primer according to any one of the first aspect to the fourth aspect, in which the metal fine particle (b) is a fine particle of at least one selected from the group consisting of iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), palladium (Pd), silver (Ag), tin (Sn), platinum (Pt), and gold (Au).

[0015] According to a sixth aspect, the present invention relates to the primer according to the fifth aspect, in which the metal fine particle (b) is a palladium fine particle.

[0016] According to a seventh aspect, the present invention relates to the primer according to the fifth aspect or the sixth aspect, in which the metal fine particle (b) is a fine particle having an average particle diameter of 1 to 100 nm.

[0017] According to an eighth aspect, the present invention relates to the primer according to any one of the first aspect to the seventh aspect, in which the alkoxysilane (c) is a compound of Formula [4]:

$$\textbf{Z-L-Si(R}^6\textbf{)}_a\textbf{(OR}^7\textbf{)}_{3-a} \qquad \textbf{[4]}$$

(where R^6 is a C_{1-6} alkyl group or a phenyl group; R7 are each independently a methyl group or an ethyl group; L is a C_{1-6} alkylene group optionally containing an ether bond; Z is an amino group optionally substituted with an aliphatic group, or an epoxy group; and a is 0 or 1).

[0018] According to a ninth aspect, the present invention relates to a priming layer for electroless plating, obtained by forming a layer of the primer as described in any one of the first aspect to the eighth aspect.

[0019] According to a tenth aspect, the present invention relates to a metal plating film, formed on the priming layer by performing electroless plating on the priming layer for electroless plating as described in the ninth aspect.

[0020] According to an eleventh aspect, the present invention relates to a metal-coated base material comprising: a base material; the priming layer for electroless plating as described in the ninth aspect formed on the base material; and the metal plating film as described in the tenth aspect formed on the priming layer for electroless plating.

[0021] According to a twelfth aspect, the present invention relates to a method for producing a metal-coated base material, the method comprising: a process A: coating a base material with the primer as described in any one of the first aspect to the eighth aspect to form a priming layer; and a process B: immersing the base material having the priming layer in an electroless plating bath to form a metal plating film.

Effect of the Invention

[0022] The primer of the present invention can form a priming layer for electroless metal plating easily by only applying on a base material. The primer of the present invention can form a priming layer having excellent adhesion to the base material. Furthermore, the primer of the present invention can provide a fine line having a width in micrometers order, which makes the primer suitable for various wiring technologies.

[0023] Also, a metal plating film can be easily formed by only immersing a priming layer for electroless metal plating formed from the primer of the present invention in an electroless plating bath, and a metal-coated base material comprising a base material, a priming layer, and a metal plating film can be easily obtained.

[0024] The metal plating film has excellent adhesion to the underlying priming layer.

[0025] Namely, the primer of the present invention may be used to form a priming layer on a base material, which leads to the formation of a so-called metal plating film having excellent adhesion to the base material.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026]

[FIG. 1] FIG. 1 shows a ^{1}H NMR spectrum of a hyperbranched polymer having a chlorine atom at a molecular terminal (HPS-Cl) obtained in Synthesis Example 1.

[FIG. 2] FIG. 2 shows a ^{13}C NMR spectrum of a hyperbranched polymer having a trioctylammonium group at a molecular terminal (HPS-$NOct_3Cl$) obtained in Synthesis Example 2.

[FIG. 3] FIG. 3 shows a ^{13}C NMR spectrum of a hyperbranched polymer having a dimethyl(octyl)ammonium group at a molecular terminal (HPS-$N(Me)_2OctCl$) obtained in Synthesis Example 4.

[FIG. 4] FIG. 4 shows an electron microscope image of a metal plating film on a PI film obtained in Example 20.

[FIG. 5] FIG. 5 shows a sectional scanning electron microscope (SEM) image of the metal plating film on the PI film obtained in Example 20.

MODES FOR CARRYING OUT THE INVENTION

[0027] The present invention will be described in detail.

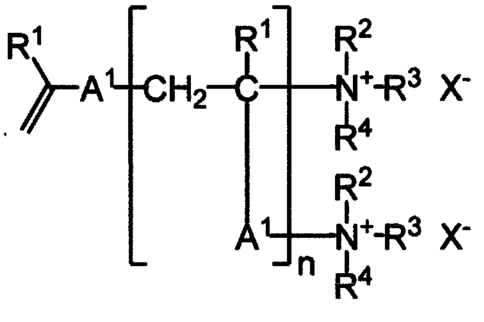
[0028] The primer of the present invention comprises (a) a hyperbranched polymer having an ammonium group and a weight-average molecular weight of 500 to 5,000,000, (b) metal fine particles, and (c) an alkoxysilane having an amino group optionally substituted with an aliphatic group, or an epoxy group, or an oligomer of the alkoxysilane.

[0029] The primer of the present invention is suitably used as a primer for forming a metal plating film on a base material by electroless plating.

[Primer]

<(a) Hyperbranched polymer>

[0030] The hyperbranched polymer for use in the primer of the present invention is a polymer having an ammonium group at a molecular terminal and a weight-average molecular weight of 500 to 5,000,000. Specific examples thereof include a hyperbranched polymer of Formula [1]:



[1]

[0031] In Formula [1], R^1 are each independently a hydrogen atom or a methyl group.

[0032] R^2 to R^4 are each independently a hydrogen atom, a linear, branched, or cyclic alkyl group having a carbon atom number of 1 to 20, a C_{7-20} arylalkyl group, or $-(CH_2CH_2O)_mR^5$ (where R^5 is a hydrogen atom or a methyl group; and m is an arbitrary integer of 2 to 100). The alkyl group and the arylalkyl group are optionally substituted with an alkoxy group, a hydroxy group, an ammonium group, a carboxy group, or a cyano group. Alternatively, two groups of R^2 to R^4 together represent a linear, branched, or cyclic alkylene group, or R^2 to R^4 together with the nitrogen atom to which R^2 to R^4 are bonded may form a ring.

[0033] X- is an anion, and n is the number of repeating unit structures and an integer of 5 to 100,000.

[0034] Preferably, examples of the linear C_{1-20} alkyl group in R^2 to R^4 include a methyl group, ethyl group, n-propyl group, n-butyl group, n-pentyl group, n-hexyl group, n-heptyl group, n-octyl group, n-nonyl group, n-decyl group, n-undecyl group, n-dodecyl group, n-tridecyl group, n-tetradecyl group, n-pentadecyl group, n-hexadecyl group, n-heptadecyl group, n-octadecyl group, n-nonadecyl group, and n-eicosyl group. A group having eight or more carbon atoms is preferred because the primer with such a group is sparingly soluble in an electroless plating solution and, in particular, an n-octyl group is preferred. Examples of the branched alkyl group include an isopropyl group, isobutyl group, sec-butyl group, and tert-butyl group. Examples of the cyclic alkyl group include groups having a cyclopentyl ring or cyclohexyl ring structure.

[0035] Examples of the C_{7-20} arylalkyl group in R^2 to R^4 include a benzyl group and phenethyl group.

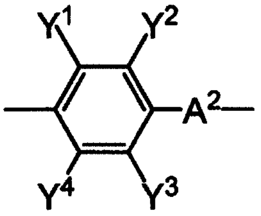
[0036] Examples of the linear alkylene group that two groups of R^2 to R^4 together form include a methylene group, ethylene group, n-propylene group, n-butylene group, and n-hexylene group. Examples of the branched alkylene group include an isopropylene group, isobutylene group, and 2-methylpropylene group. Examples of the cyclic alkylene group include monocyclic, multicyclic, bridged cyclic C_{3-30} alicyclic aliphatic groups. Specific examples thereof include groups having four or more carbon atoms and monocyclic, bicyclic, tricyclic, tetracyclic, or pentacyclic structures. These alkylene groups may contain a nitrogen atom, a sulfur atom, or an oxygen atom in the groups.

[0037] The ring that R^2 to R^4 together with the nitrogen atom to which R^2 to R^4 are bonded form in the structure of Formula [1] may contain a nitrogen atom, a sulfur atom, or an oxygen atom in the ring, and examples thereof include a pyridine ring, pyrimidine ring, pyrazine ring, quinoline ring, and bipyridyl ring.

[0038] Preferable examples of the combination of R^2 to R^4 include [methyl group, methyl group, methyl group], [methyl group, methyl group, ethyl group], [methyl group, methyl group, n-butyl group], [methyl group, methyl group, n-hexyl group], [methyl group, methyl group, n-octyl group], [methyl group, methyl group, n-decyl group], [methyl group, methyl group, n-dodecyl group], [methyl group, methyl group, n-tetradecyl group], [methyl group, methyl group, n-hexadecyl group], [methyl group, methyl group, n-octadecyl group], [ethyl group, ethyl group, ethyl group], [n-butyl group, n-butyl group, n-butyl group], [n-hexyl group, n-hexyl group, n-hexyl group], and [n-octyl group, n-octyl group, n-octyl group]. Among them, the combinations of [methyl group, methyl group, n-octyl group] and [n-octyl group, n-octyl group, n-octyl group] are preferable.

[0039] Preferable examples of the anion X- include a halogen atom, PF_6^-, BF_4^-, or a perfluoroalkane sulfonate.

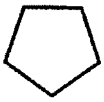
[0040] In Formula [1], A^1 is a structure of Formula [2]:

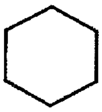

[2]

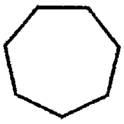
[0041] In Formula [2], A^2 is a linear, branched, or cyclic alkylene group having a carbon atom number of 1 to 30 optionally containing an ether bond or an ester bond.

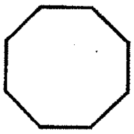
[0042] Y^1 to Y^4 are each independently a hydrogen atom, a C_{1-20} alkyl group, a C_{1-20} alkoxy group, a nitro group, a hydroxy group, an amino group, a carboxy group, or a cyano group.

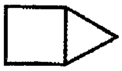
[0043] Specific examples of the alkylene group of A^2 include linear alkylene groups such as a methylene group, ethylene group, n-propylene group, n-butylene group, and n-hexylene group, and branched alkylene groups such as an isopropylene group, isobutylene group, and 2-methylpropylene group. Examples of the cyclic alkylene group include monocyclic, multicyclic, and bridged cyclic C_{3-30} alicyclic aliphatic groups. Specific examples thereof include groups having four or more carbon atoms and monocyclic, bicyclic, tricyclic, tetracyclic, pentacyclic structures. For example, structural examples of the alicyclic moieties (a) to (s) in the alicyclic aliphatic groups are shown below:

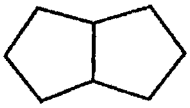

(a)

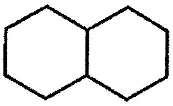

(b)

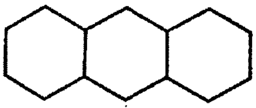

(c)

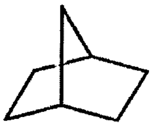

(d)

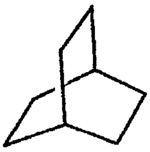

(e)


(f)

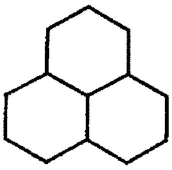

(g)

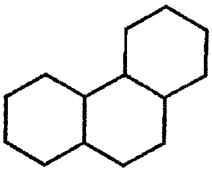

(h)

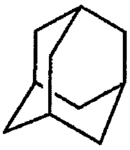

(i)

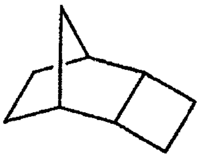

(j)

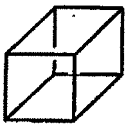

(k)

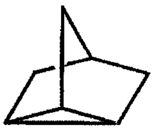

(l)


(m)

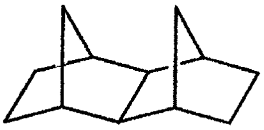

(n)


(o)

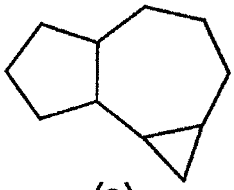

(p)



(q)



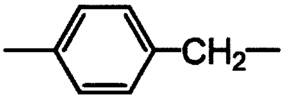
(r)



(s)

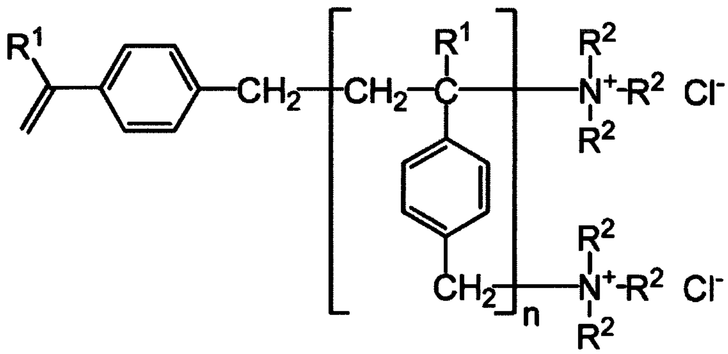
[0044] In Formula [2] above, examples of the C_{1-20} alkyl group of Y^1 to Y^4 include a methyl group, ethyl group, isopropyl group, cyclohexyl group, and n-pentyl group. Examples of the C_{1-20} alkoxy group include a methoxy group, ethoxy group, isopropoxy group, cyclohexyloxy group, and n-pentyloxy group. Y^1 to Y^4 are preferably each independently a hydrogen atom or a C_{1-20} alkyl group.

[0045] Preferably, A^1 is a structure of Formula [5]:



[5]

[0046] Examples of the hyperbranched polymer for use in the present invention include a hyperbranched polymer of Formula [3]:



[3]

[0047] In Formula [3], R^1, R^2, and n have the same meanings as described above.

[0048] A hyperbranched polymer for use in the present invention having an ammonium group at a molecular terminal can be obtained, for example, by allowing a hyperbranched polymer having a halogen atom at a molecular terminal to react with an amine compound.

[0049] A hyperbranched polymer having a halogen atom at a molecular terminal can be produced from a hyperbranched polymer having a dithiocarbamate group at a molecular terminal according to the description of WO 2008/029688 Pamphlet. The hyperbranched polymer having a dithiocarbamate group at a molecular terminal is commercially available and HYPERTECH (registered trademark) HPS-200 manufactured by NISSAN CHEMICAL INDUSTRIES, LTD. and the like can be suitably used.

[0050] Examples of the amine compound that can be used in the reaction include primary amines including aliphatic amines such as methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, isobutylamine, sec-butylamine, tert-butylamine, n-pentylamine, n-hexylamine, n-heptylamine, n-octylamine, n-nonylamine, n-decylamine, n-undecylamine, n-dodecylamine, n-tridecylamine, n-tetradecylamine, n-pentadecylamine, n-hexadecylamine, n-heptadecylamine, n-octadecylamine, n-nonadecylamine, and n-eicosylamine; alicyclic amines such as cyclopentylamine and cyclohexylamine; aralkyl amines such as benzylamine and phenethylamine; and aromatic amines, for example, anilines such as aniline, p-n-butylaniline, p-tert-butylaniline, p-n-octylaniline, p-n-decylaniline, p-n-dodecylaniline, and p-n-tetradecylaniline, naphthylamines such as 1-naphthylamine and 2-naphthylamine, aminoanthracenes such as 1-aminoanthracene and 2-aminoanthracene, aminoanthraquinones such as 1-aminoanthraquinone, aminobiphenyls such as 4-aminobiphenyl and 2-aminobiphenyl, aminofluorenes such as 2-aminofluorene, 1-amino-9-fluorenone, and 4-amino-9-fluorenone, aminoindanes such as 5-aminoindane, aminoisoquinolines such as 5-aminoisoquinoline, and aminophenanthrenes such as 9-aminophenanthrene. Further examples thereof include amine compounds such as N-(tert-butoxycarbonyl)-1,2-ethylenediamine, N-(tert-butoxycarbonyl)-1,3-propylenediamine, N-(tert-butoxycarbonyl)-1,4-butylenediamine, N-(tert-butoxycarbonyl)-1,5-pentamethylenediamine, N-(tert-butoxycarbonyl)-1,6-hexamethylenediamine, N-(2-hydroxyethyl)amine, N-(3-hydroxypropyl)amine, N-(2-methoxyethyl)amine, and N-(2-ethoxyethyl)amine.

[0051] Examples of secondary amines include aliphatic amines such as dimethylamine, diethylamine, di-n-propylamine, diisopropylamine, di-n-butylamine, diisobutylamine, di-sec-butylamine, di-n-pentylamine, ethylmethylamine, methyl-n-propylamine, methyl-n-butylamine, methyl-n-pentylamine, ethylisopropylamine, ethyl-n-butylamine, ethyl-n-pentylamine, methyl-n-octylamine, methyl-n-decylamine, methyl-n-dodecylamine, methyl-n-tetradecylamine, methyl-n-hexadecylamine, methyl-n-octadecylamine, ethylisopropylamine, ethyl-n-octylamine, di-n-hexylamine, di-n-octylamine, di-n-dodecylamine, di-n-hexadecylamine, and di-n-octadecylamine; alicyclic amines such as dicyclohexylamine; aralkyl amines such as dibenzylamine; aromatic amines such as diphenylamine; and nitrogen-containing heterocyclic compounds such as phthalimide, pyrrole, piperidine, piperazine, and imidazole. Further examples thereof include bis(2-hydroxyethyl)amine, bis(3-hydroxypropyl)amine, bis(2-ethoxyethyl)amine, and bis(2-propoxyethyl)amine.

[0052] Examples of tertiary amines include aliphatic amines such as trimethylamine, triethylamine, tri-n-propylamine, tri-n-butylamine, tri-n-pentylamine, tri-n-hexylamine, tri-n-octylamine, tri-n-dodecylamine, dimethyl(ethyl)amine, dimethyl-n-butylamine, dimethyl-n-hexylamine, dimethyl-n-octylamine, dimethyl-n-decylamine, diethyl-n-decylamine, dimethyl-n-dodecylamine, dimethyl-n-tetradecylamine, dimethyl-n-hexadecylamine, dimethyl-n-octadecylamine, and dimethyl-n-eicosylamine; and nitrogen-containing heterocyclic compounds such as pyridine, pyrazine, pyrimidine, quinoline, 1-methylimidazole, 4,4’-bipyridyl, and 4-methyl-4,4’-bipyridyl.

[0053] The amine compound can be used in the reaction in 0.1 to 20 molar equivalents, preferably 0.5 to 10 molar equivalents, and more preferably 1 to 5 molar equivalents per mole of halogen atom of the hyperbranched polymer having a halogen atom at a molecular terminal.

[0054] The reaction between the hyperbranched polymer having a halogen atom at a molecular terminal and the amine compound can be carried out in water or an organic solvent in the presence or absence of a base. The solvent used is preferably capable of dissolving the hyperbranched polymer having a halogen atom at a molecular terminal and the amine compound. A solvent capable of dissolving the hyperbranched polymer having a halogen atom at a molecular terminal and the amine compound and incapable of dissolving a hyperbranched polymer having an ammonium group at a molecular terminal would be more suitable for easy isolation.

[0055] Any solvent may be used in the reaction, provided the solvent does not substantially inhibit the reaction from proceeding, and examples thereof include water; alcohols such as isopropanol; organic acids such as acetic acid; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, and 1,2-dichlorobenzene; ethers such as tetrahydrofuran (THF) and diethyl ether; ketones such as acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), and cyclohexanone; halides such as chloroform, dichloromethane, and 1,2-dichloroethane; aliphatic hydrocarbons such as n-hexane, n-heptane, and cyclohexane; and amides such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide, and N-methyl-2-pyrrolidone (NMP). These solvents may be used singly or in combination of two or more thereof. The mass of the solvent used is 0.2 to 1,000 times, preferably 1 to 500 times, more preferably 5 to 100 times, and most preferably 5 to 50 times the mass of the hyperbranched polymer having a halogen atom at a molecular terminal.

[0056] As a suitable base, commonly used are inorganic compounds including alkali metal hydroxides and alkaline-earth metal hydroxides (for example, sodium hydroxide, potassium hydroxide, calcium hydroxide), alkali metal oxides and alkaline-earth metal oxides (for example, lithium oxide, calcium oxide), alkali metal hydrides and alkaline-earth metal hydrides (for example, sodium hydride, potassium hydride, calcium hydride), alkali metal amides (for example, sodium amide), alkali metal carbonates and alkaline-earth metal carbonates (for example, lithium carbonate, sodium carbonate, potassium carbonate, calcium carbonate), and alkali metal bicarbonates (for example, sodium bicarbonate), and organometallic compounds including alkali metal alkyls, alkyl magnesium halides, alkali metal alkoxides, alkaline-earth metal alkoxides, and dimethoxymagnesium. Potassium carbonate and sodium carbonate are particularly preferable. The base is used in 0.2 to 10 molar equivalents, preferably 0.5 to 10 molar equivalents, and most preferably 1 to 5 molar equivalents per mole of halogen atom of the hyperbranched polymer having a halogen atom at a molecular terminal.

[0057] Oxygen in the reaction system is preferably thoroughly removed before this reaction is started and inert gases such as nitrogen and argon may be used to purge air from the system. The reaction condition is suitably selected from the reaction time range of 0.01 to 100 hours and the reaction temperature range of 0 to 300°C. Preferably, the reaction time is 0.1 to 72 hours and the reaction temperature is 20 to 150°C.

[0058] When a tertiary amine is used, the hyperbranched polymer of Formula [1] can be obtained whether or not a base is present.

[0059] When a primary amine or a secondary amine compound is reacted with a hyperbranched polymer having a halogen atom at a molecular terminal in the absence of a base, a hyperbranched polymer with a terminal ammonium group, in which respectively corresponding secondary amine terminal group or tertiary amine terminal group of hyperbranched polymer is protonated can be obtained. Even when a base is used in the reaction, the reactants may be mixed with an aqueous solution of an acid such as hydrogen chloride, hydrogen bromide, and hydrogen iodide in an organic solvent to obtain a corresponding hyperbranched polymer with a terminal ammonium group, in which respectively corresponding secondary amine terminal group or tertiary amine terminal group of hyperbranched polymer is protonated.

[0060] The weight-average molecular weight Mw of the hyperbranched polymer measured by gel permeation chromatography in terms of polystyrene is 500 to 5,000,000, preferably 1,000 to 500,000, more preferably 2,000 to 200,000, and most preferably 3,000 to 100,000. The degree of distribution: Mw (weight-average molecular weight)/ Mn (number-average molecular weight) is 1.0 to 7.0, preferably 1.1 to 6.0, and more preferably 1.2 to 5.0.

<(b) Metal fine particles>

[0061] The metal fine particles for use in the primer of the present invention are not specifically limited, and examples of metal species include iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), palladium (Pd), silver (Ag), tin (Sn), platinum (Pt), and gold (Au). These metals may be used singly, or an alloy of two or more metals may be used. Among these metals, palladium fine particles are included as suitable metal fine particles. Oxides of the metals may also be used as metal fine particles.

[0062] The metal fine particles are obtained by reduction of a metal ion, for example, by irradiating an aqueous solution of a metal salt with a high-pressure mercury lamp or adding to the aqueous solution a compound having a reducing action (so-called reducing agent). For example, a metal ion may be reduced by, for example, adding an aqueous solution of a metal salt to a solution in which the hyperbranched polymer is dissolved and irradiating the resultant mixture with ultraviolet light or adding an aqueous solution of a metal salt and a reducing agent to the solution, to form a complex of the hyperbranched polymer and the metal fine particles concurrently with the preparation of a primer comprising the hyperbranched polymer and the metal fine particles.

[0063] Examples of the metal salt include chloroauric acid, silver nitrate, copper sulfate, copper nitrate, copper acetate, tin chloride, platinous chloride, chloroplatinic acid, $Pt(dba)_2$[dba=dibenzylideneacetone], $Pt(cod)_2$[cod=1,5-cyclooctadiene], $Pt(CH_3)_2(cod)$, palladium chloride, palladium acetate ($Pd(OC(=O)CH_3)_2$), palladium nitrate, $Pd_2(dba)_3\text{-}CHCl_3$, $Pd(dba)_2$, rhodium chloride, rhodium acetate, ruthenium chloride, ruthenium acetate, Ru(cod)(cot)[cot = cyclooctatriene], iridium chloride, iridium acetate, and $Ni(cod)_2$.

[0064] The reducing agent is not specifically limited, and various reducing agents may be used. A reducing agent is preferably selected depending on the metal species added in the intended primer and other factors. Examples of the reducing agent that can be used include metal borohydrides such as sodium borohydride and potassium borohydride; aluminum hydrides such as lithium aluminum hydride, potassium aluminum hydride, cesium aluminum hydride, beryllium aluminum hydride, magnesium aluminum hydride, and calcium aluminum hydride; hydrazine compounds; citric acid and salts thereof; succinic acid and salts thereof; ascorbic acid and salts thereof; primary or secondary alcohols such as methanol, ethanol, isopropanol, and polyol; tertiary amines such as trimethylamine, triethylamine, diisopropyl(ethyl)amine, diethylmethylamine, tetramethylethylenediamine [TMEDA], and ethylenediaminetetraacetic acid [EDTA]; hydroxylamines; and phosphines such as tri-n-propylphosphine, tri-n-butylphosphine, tricyclohexylphosphine, tribenzylphosphine, triphenylphosphine, triethoxyphosphine, 1,2-bis(diphenylphosphino)ethane [DPPE], 1,3-bis(diphenylphosphino)propane [DPPP], 1,1'-bis(diphenylphosphino)ferrocene [DPPF], and 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl [BINAP].

[0065] The average particle diameter of the metal fine particles is preferably 1 to 100 nm. The reason is that, with an average particle diameter exceeding 100 nm, the surface areas of the metal fine particles decrease, resulting in the decrease in the catalytic activity. The average particle diameter is more preferably 75 nm or less and particularly preferably 1 to 30 nm.

[0066] The hyperbranched polymer (a) is preferably used for the primer of the present invention in an amount of 50 to 2,000 parts by mass relative to 100 parts by mass of the metal fine particles (b). If the amount is less than 50 parts by mass, the metal fine particles are insufficiently dispersed, and if the amount exceeds 2,000 parts by mass, the organic content becomes high, leading to problems affecting properties and the like. The amount of the hyperbranched polymer is more preferably 100 to 1,000 parts by mass.

<(c) Alkoxysilane or oligomer thereof>

[0067] The alkoxy silane or an oligomer thereof for use in the primer of the present invention (hereinafter, also simply called an "alkoxysilane" in the specification) is any alkoxysilane having an amino group optionally substituted with an aliphatic group or an epoxy group, or an oligomer thereof.

[0068] Examples of the alkoxysilane having an amino group optionally substituted with an aliphatic group include silane compounds having one or more amino groups optionally substituted with an aliphatic group in one molecule and having an alkoxysilyl group.

[0069] Examples of the alkoxysilane having an epoxy group include silane compounds having one or more epoxy groups in one molecule and having an alkoxysilyl group.

[0070] Preferable examples of the alkoxysilane for use in the primer of the present invention include a compound of Formula [4]:

$$\text{Z-L-Si}(R^6)_a(OR^7)_{3-a} \qquad [4]$$

[0071] In Formula [4], R^6 is a C_{1-6} alkyl group or a phenyl group; R^7 are each independently a methyl group or an ethyl group; L is a C_{1-6} alkylene group optionally containing an ether bond; Z is an amino group optionally substituted with an aliphatic group, or an epoxy group; and a is 0 or 1.

[0072] Examples of the C_{1-6} alkyl group in R^6 include a methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, sec-butyl group, tert-butyl group, n-hexyl group, and cyclohexyl group.

[0073] Among them, a methyl group is preferable.

[0074] Examples of the C_{1-6} alkylene group optionally containing an ether bond in L include a methylene group, ethylene group, trimethylene group, methylethylene group, tetramethylene group, 1-methyltrimethylene group, pentamethylene group, 2,2-dimethyltrimethylene group, hexamethylene group, 2-oxabutane-1,4-diyl group, 2-oxapentane-1,5-diyl group, 3-oxapentane-1,5-diyl group, and 2-oxahexane-1,6-diyl group.

[0075] Among them, an ethylene group, trimethylene group, and 2-oxapentane-1,5-diyl group are preferable.

[0076] Examples of the amino group optionally substituted with an aliphatic group in Z include an amino group, methylamino group, ethylamino group, 2-aminoethylamino group, diethylamino group, propylamino group, 3-trimethoxysilylpropylamino group, 3-triethoxysilylpropylamino group, and 1-methylpentylideneamino group.

[0077] Among them, an amino group, 2-aminoethylamino group, and 3-trimethoxysilylpropylamino group are preferable.

[0078] Examples of the alkoxysilane include alkoxysilanes having an amino group such as 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-aminopropyl(dimethoxy)(methyl)silane, 3-aminopropyl(diethoxy)(methyl)silane, 3-aminopropyl(diethoxy)(ethyl)silane, 3-(1-methylpentylideneamino)propyltrimethoxysilane, 3-(2-aminoethylamino)propyltrimethoxysilane, 3-(2-aminoethylamino)propyl(dimethoxy)(methyl)silane, and bis[3-trimethoxysilylpropyl]amine; alkoxysilanes having an epoxy group such as 3-(glycidyloxy)propyltrimethoxysilane, 3-(glycidyloxy)propyltriethoxysilane, dimethoxy(3-(glycidyloxy)propyl)(methyl)silane, diethoxy(3-(glycidyloxy)propyl)(methyl)silane, diethoxy(ethyl)(3-(glycidyloxy)propyl)silane, and 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane; and oligomers of the above alkoxysilanes such as amino group/methyl group containing methoxysilane oligomers and epoxy group/methyl group containing methoxysilane oligomers. These alkoxysilanes may be used singly, or two or more alkoxysilanes may be used in combination.

[0079] The alkoxysilane (c) is preferably used for the primer of the present invention in an amount of 1 to 2,000 parts by mass relative to 100 parts by mass of a complex formed of the hyperbranched polymer and the metal fine particles described below. If the amount is 1 part by mass or more, superior base material adhesion can be obtained. If the amount is 2,000 parts or less, superior platability can be obtained. The amount is more preferably 5 to 1,000 parts by mass.

<Primer>

[0080] The primer of the present invention comprises the hyperbranched polymer (a) having an ammonium group at a molecular terminal, the metal fine particles (b), and the alkoxysilane (c) having an amino group optionally substituted with an aliphatic group or an epoxy group, or an oligomer thereof, in which the hyperbranched polymer and the metal fine particles preferably form a complex.

[0081] As used herein, the term complex means a state in which the hyperbranched polymer coexists with the metal fine particles so as to be in contact with or in proximity to the metal fine particles through the action of the ammonium group at the terminal of the hyperbranched polymer to form a particulate form. In other words, the complex has a structure in which the ammonium group of the hyperbranched polymer is attached to or coordinates with the metal fine particles.

[0082] Accordingly, the "complex" in the present invention includes a complex in which the metal fine particles and the hyperbranched polymer are bonded to form a complex as well as a complex in which the metal fine particles and the hyperbranched polymer exist independently without forming bonds.

[0083] The formation of a complex of the hyperbranched polymer having an ammonium group and the metal fine particles is performed concurrently with the preparation of the primer comprising the hyperbranched polymer and the metal fine particles. Examples of the method include a method in which metal fine particles stabilized to a certain degree with a lower ammonium ligand are synthesized and the ligand is exchanged with the hyperbranched polymer and a method in which a metal ion is directly reduced in a solution of the hyperbranched polymer having an ammonium group to form a complex. Examples thereof include a method in which an aqueous solution of a metal salt is added to a solution in which the hyperbranched polymer is dissolved and the resultant mixture is irradiated with ultraviolet light or a method in which an aqueous solution of a metal salt and a reducing agent are added to the solution to reduce the metal ion to form a complex.

[0084] In the ligand exchange method, the raw material that is metal fine particles stabilized to a certain degree with a lower ammonium ligand can be synthesized by the method described in Journal of Organometallic Chemistry 1996, 520, 143 to 162, etc. A hyperbranched polymer having an ammonium group is dissolved in the resultant reaction mixture of the metal fine particles, and the mixture is stirred at room temperature (approximately 25°C) or stirred with heating to obtain the intended metal fine particle complex.

[0085] Any solvent may be used, provided the solvent is capable of dissolving the metal fine particles and the hyperbranched polymer having an ammonium group at the necessary concentrations or more. Specific examples thereof include alcohols such as ethanol, n-propanol, and isopropanol; halogenated hydrocarbons such as methylene chloride and chloroform; cyclic ethers such as tetrahydrofuran (THF), 2-methyltetrahydrofuran, and tetrahydropyran; nitriles such as acetonitrile and butyronitrile, and a mixture of these solvents. Preferably, tetrahydrofuran is used.

[0086] The temperature at which the reaction mixture of the metal fine particles and the hyperbranched polymer having an ammonium group are mixed may be generally from 0°C to the boiling point of the solvent, and preferably in a range of room temperature (approximately 25°C) to 60°C.

[0087] In the ligand exchange method, a phosphine dispersant (phosphine ligand) may be used instead of the amine dispersant (lower ammonium ligand) to stabilize metal fine particles to a certain degree beforehand.

[0088] The direct reduction method involves dissolving a metal ion and a hyperbranched polymer having an ammonium group in a solvent and reduction is performed with a primary or secondary alcohol such as methanol, ethanol, isopropanol, and polyols to obtain the intended metal fine particle complex.

[0089] The source of the metal ion used includes the above described metal salts.

[0090] Any solvent may be used, provided the solvent is capable of dissolving the metal ion and the hyperbranched polymer having an ammonium group to the necessary concentrations or more. Specific examples thereof include alcohols such as methanol, ethanol, propanol, and isopropanol; halogenated hydrocarbons such as methylene chloride and chloroform; cyclic ethers such as tetrahydrofuran (THF), 2-methyltetrahydrofuran, and tetrahydropyran; nitriles such as acetonitrile and butyronitrile; amides such as N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP); sulfoxides such as dimethylsulfoxide, and mixed solutions of these solvents. Preferably, alcohols, halogenated hydrocarbons, and cyclic ethers are used. More preferably, ethanol, isopropanol, chloroform, and tetrahydrofuran are used.

[0091] The temperature for the reduction reaction can be generally within the range of 0°C to the boiling point of the solvents and is preferably within the range of room temperature (approximately 25°C) to 60°C.

[0092] As another direct reduction method, by dissolving a metal ion and a hyperbranched polymer having an ammonium group in a solvent and allowing the ingredients to react under hydrogen atmosphere, the intended metal fine particle complex can be obtained.

[0093] The source of the metal ion used includes the above described metal salts and metal carbonyl complexes such as hexacarbonylchromium [$Cr(CO)_6$], pentacarbonyliron [$Fe(CO)_5$], octacarbonyldicobalt [$Co_2(CO)_8$], and tetracarbonylnickel [$Ni(CO)_4$]. Zero-valent metal complexes such as metal olefin complexes, metal phosphine complexes, and metal nitrogen complexes may also be used.

[0094] Any solvent may be used, provided the solvent is capable of dissolving the metal ion and the hyperbranched polymer having an ammonium group to the necessary concentrations or more. Specific examples thereof include alcohols such as ethanol and propanol; halogenated hydrocarbons such as methylene chloride and chloroform; cyclic ethers such as tetrahydrofuran, 2-methyltetrahydrofuran, and tetrahydropyran; nitriles such as acetonitrile and butyronitrile, and a mixture of these solvents. Preferably, tetrahydrofuran is used.

[0095] The temperature at which the metal ion and the hyperbranched polymer having an ammonium group are mixed may be generally from 0°C to the boiling point of the solvent.

[0096] As the direct reduction method, a metal ion and a hyperbranched polymer having an ammonium group may also be dissolved in a solvent and subjected to thermal decomposition to obtain the intended metal fine particle complex.

[0097] The source of the metal ion used includes the above described metal salts, metal complexes such as metal carbonyl complexes and other zero-valent metal complexes, and metal oxides such as silver oxide.

[0098] Any solvent may be used, provided the solvent is capable of dissolving the metal ion and the hyperbranched polymer having an ammonium group to the necessary concentrations or more. Specific examples thereof include alcohols such as methanol, ethanol, n-propanol, isopropanol, and ethylene glycol; halogenated hydrocarbons such as methylene chloride and chloroform; cyclic ethers such as tetrahydrofuran (THF), 2-methyltetrahydrofuran, and tetrahydropyran; nitriles such as acetonitrile and butyronitrile; aromatic hydrocarbons such as benzene and toluene, and a mixture of these solvents. Preferably, toluene is used.

[0099] The temperature at which the metal ion and the hyperbranched polymer having an ammonium group are mixed may be generally from 0°C to the boiling point of the solvent. The temperature is preferably close to the boiling point of the solvent, for example, 110°C (heating at reflux) in the case of toluene.

[0100] The complex of the hyperbranched polymer having an ammonium group and the metal fine particles thus obtained can be formed as a solid such as powder after purification such as reprecipitation.

[0101] The primer of the present invention may be in the form of varnish that comprises the hyperbranched polymer (a) having an ammonium group, the metal fine particles (b) (preferably a complex formed from these ingredients), and the alkoxysilane (c) (or an oligomer of the alkoxysilane) and that is used for forming [a priming layer for electroless plating] as described below.

<Thickeners>

[0102] The primer of the present invention may contain thickeners as needed to adjust the viscosity and rheological characteristics of the primer. The addition of the thickeners therefore serves a particularly important role when the primer of the present invention is used as printing ink.

[0103] Examples of the thickeners include poly(acrylic acid)s (including cross-linked ones) such as carboxyvinyl polymers (carbomers); vinyl polymers such as poly(vinyl pyrrolidone) (PVP), poly(vinyl alcohol) (PVA), poly(vinyl acetate) (PVAc) and polystyrene (PS); poly(ethylene oxide)s; polyesters; polycarbonates; polyamides; polyurethanes; polysaccharides such as dextrin, agar, carrageenan, alginic acid, gum arabic, guar gum, gum traganth, locust bean gum, starch, pectin, carboxymethylcellulose, hydroxyethylcellulose, and hydroxypropylcellulose; and proteins such as gelatin and casein. The polymers include not only homopolymers but also copolymers. These thickeners may be used singly, or two or more thickeners may be used in combination.

<Other additives>

[0104] The primer of the present invention may further appropriately contain additives such as surfactants and various kinds of surface conditioners as long as the effect of the present invention is not impaired.

[0105] Examples of the surfactants include polyoxyethylene alkyl ethers such as polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene cetyl ether, and polyoxyethylene oleyl ether; polyoxyethylene alkylaryl ethers such as polyoxyethylene octylphenyl ether and polyoxyethylene nonylphenyl ether; polyoxyethylene-polyoxypropylene block copolymers; sorbitan fatty acid esters such as sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, sorbitan monooleate, sorbitan tristearate, and sorbitan trioleate; polyoxyethylene nonionic surfactants such as polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate, and polyoxyethylene sorbitan trioleate; fluorine-based surfactants such as EFTOP (registered trademark) EF-301, EF-303, and EF-352 [manufactured by Mitsubishi Materials Electronic Chemicals Co., Ltd.], MEGAFAC (registered trademark) F-171, F-173, R-08, and R-30 [manufactured by DIC Corporation], Novec (registered trademark) FC-430 and FC-431 [manufactured by Sumitomo 3M Ltd.], ASAHI GUARD (registered trademark) AG-710 [manufactured by Asahi Glass Co., Ltd.], and SURFLON (registered trademark) S-382 [manufactured by AGC Seimi Chemical Co., Ltd.].

[0106] Examples of the surface conditioners include silicone-based leveling agents such as Shin-Etsu Silicone (registered trademark) KP-341 [manufacture by Shin-Etsu Chemical Co., Ltd.]; and silicone-based surface conditioners such as BYK (registered trademark) -302, BYK -307, BYK -322, BYK -323, BYK -330, BYK -333, BYK -370, BYK -375, and BYK -378 [manufactured by BYK Japan KK].

[0107] These additives may be used singly, or two or more additives may be used in combination. The additives are used in an amount of preferably 0.001 to 50 parts by mass, more preferably 0.005 to 10 parts by mass, and even more preferably 0.01 to 5 parts by mass relative to 100 parts by mass of the complex formed of the hyperbranched polymer and the metal fine particles.

[Priming layer for electroless plating]

[0108] The primer of the present invention may be applied on a base material to form a priming layer for electroless plating. The present invention is also directed to the priming layer for electroless plating.

[0109] The base material is not specifically limited, and a nonconducting base material or a conducting base material may be preferably used.

[0110] Examples of the nonconducting base material include glass, ceramics; polyethylene resin, polypropylene resin, vinyl chloride resin, nylon (polyamide resin), polyimide resin, polycarbonate resin, acrylic resin, PEN (poly(ethylene naphthalate)) resin, PET (poly(ethylene terephthalate)) resin, PEEK (polyetheretherketone) resin, ABS (acrylonitrile-butadiene-styrene copolymer) resin, epoxy resin, and polyacetal resin; and paper. The nonconducting base material is suitably used in the form of sheet, film, or the like, and the thickness is not specifically limited.

[0111] Examples of the conducting base material include metals such as ITO (tin-doped indium oxide), ATO (antimony-doped tin oxide), FTO (fluorine-doped tin oxide), AZO (aluminum-doped zinc oxide), GZO (gallium-doped zinc oxide), various stainless steels, aluminum and aluminum alloys such as duralumin, iron and iron alloys, copper and copper alloys such as brass, phosphor bronze, cupronickel, and beryllium copper, nickel and nickel alloys, and silver and silver alloys such as nickel silver.

[0112] Furthermore, a base material is also usable in which a thin film of any of these conducting base material is formed on the nonconducting base material.

[0113] The base material may also be a three-dimensional molded body.

[0114] The specific method to form a priming layer for electroless plating from the primer comprising the hyperbranched polymer having an ammonium group, the metal fine particles, and the alkoxysilane involves dissolving or dispersing the hyperbranched polymer having an ammonium group, the metal fine particles (preferably a complex formed from these ingredients), and the alkoxysilane in a suitable solvent to form a varnish, coating a base material on which a metal plating coating film is to be formed with the varnish by spin coating; blade coating; dip coating; roll coating; bar coating; die coating; spray coating; ink jet method; pen lithography such as fountain-pen nanolithography (FPN) and dip-pen nanolithography (DPN); relief printing such as letterpress printing, flexography, resin relief printing, contact printing, microcontact printing (μCP), nanoimprinting lithography (NIL), and nanotransfer printing (nTP); intaglio printing such as gravure printing and engraving; planographic printing; stencil printing such as screen printing and mimeograph; offset printing; or the like and evaporating the solvent to be dried to form a thin layer.

[0115] Among these coating methods, spin coating, spray coating, ink jet method, pen lithography, contact printing, μCP, NIL, and nTP are preferred. Spin coating has advantages in that a highly volatile solution can be used because a short time is needed for coating and that a highly uniform coating can be obtained. Spray coating needs only a very small amount of vanish to obtain a highly uniform coating, which is very advantageous for industrial production. Ink jet method, pen lithography, contact printing, μCP, NIL, and nTP can form (draw), for example, fine patterns such as wiring efficiently, which is very advantageous for industrial production.

[0116] Any solvent can be used, provided the solvent dissolves or disperses the complex and the alkoxysilane, and examples thereof include water; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, chlorobenzene, and dichlorobenzene; alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, 2-butanol, n-hexanol, n-octanol, 2-octanol, and 2-ethylhexanol; cellosolves such as methyl cellosolve, ethyl cellosolve, butyl cellosolve, and phenyl cellosolve; glycol ethers such as propylene glycol monomethyl ether (PGME), propylene glycol monoethyl ether, propylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monobutyl ether, dipropylene glycol monomethyl ether, triethylene glycol monomethyl ether, tripropylene glycol monomethyl ether, ethylene glycol dimethyl ether, propylene glycol dimethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dibutyl ether, diethylene glycol ethyl methyl ether, diethylene glycol butyl methyl ether, diethylene glycol isopropyl methyl ether, dipropylene glycol dimethyl ether, triethylene glycol dimethyl ether, and tripropylene glycol dimethyl ether; glycol esters such as ethylene glycol monomethyl ether acetate, propylene glycol monomethyl ether acetate (PGMEA); ethers such as tetrahydrofuran (THF), methyltetrahydrofuran, 1,4-dioxane, diethyl ether; esters such as ethyl acetate and butyl acetate; ketones such as acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), cyclopentanone, and cyclohexanone; aliphatic hydrocarbons such as n-heptane, n-hexane, and cyclohexane; halogenated aliphatic hydrocarbons such as 1,2-dichloroethane and chloroform; amides such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), and N,N-dimethylacetamide; and dimethyl sulfoxide. These solvents may be used singly, or two or more solvents may be mixed. Glycols such as ethylene glycol, propylene glycol, and butylene glycol may be added to adjust the viscosity of the varnish. Although the concentration of the complex dissolved or dispersed in the solvent is not limited, the concentration of the complex in the varnish is 0.05 to 90% by mass and preferably 0.1 to 80% by mass.

[0117] The method for drying the solvent is not specifically limited, and, for example, a hotplate or an oven can be used to evaporate the solvent under an appropriate atmosphere, i.e., air, inert gas such as nitrogen, or in vacuum. This can provide a priming layer having a uniformly formed film surface. The heating temperature is not specifically limited, provided the solvent can be evaporated, and a temperature of 40 to 250°C is preferably used.

[Electroless plating process, metal plating film, metal-coated base material]

[0118] The priming layer for electroless plating formed on the base material thus obtained is subjected to electroless plating to form a metal plating film on the priming layer for electroless plating. The present invention is also directed to the metal plating film thus obtained as well as the metal-coated base material having on a base material a priming layer for electroless plating and a metal plating film in this order.

[0119] The electroless plating process (step) is not specifically limited, and any commonly known electroless plating process may be used. For example, the common method involves using a conventionally-known electroless plating solution and immersing a priming layer for electroless plating formed on the base material in the plating solution (bath).

[0120] The electroless plating solution mainly contains a metal ion (a metal salt), a complexing agent, and a reducing agent, and, depending on the application, a pH adjusting agent, a pH buffering agent, a reaction accelerator (a second complexing agent), a stabilizer, a surfactant (used for, for example, giving a luster to the plating film and improving wettability of the surface to be treated), and other agents are contained as appropriate.

[0121] Examples of the metal for use for the metal plating film formed by electroless plating include iron, cobalt, nickel, copper, palladium, silver, tin, platinum, gold, and alloys of these. The metal is suitably selected depending on the purpose.

[0122] The complexing agent and the reducing agent may be suitably selected depending on the metal ion.

[0123] Alternatively, a commercially available electroless plating solution may be used. For example, electroless nickel plating agent (Melplate (registered trademark) NI series) and electroless copper plating agent (Melplate (registered trademark) CU series) manufactured by Meltex Inc.; electroless nickel plating solution (ICP Nicoron (registered trademark) series), electroless copper plating solution (OPC-700 electroless copper M-K, ATS Addcopper IW), electroless tin plating solution (Substar SN-5), and electroless gold plating solution (Flash Gold 330, Self Gold OTK-IT) manufactured by Okuno Chemical Industries Co., Ltd.; electroless palladium plating solution (Pallet II) and electroless gold plating solution (Dip G series, NC Gold series) manufactured by Kojima Chemicals Co., Ltd.; electroless silver plating solution (S-DIA AG-40) manufactured by SASAKI CHEMICAL CO., LTD.; electroless nickel plating solution (SUMER (registered trademark) series, SUMER (registered trademark) KANIBLACK (registered trademark) series), and electroless palladium plating solution (S-KPD) manufactured by JAPAN KANIGEN CO., LTD.; electroless copper plating solution (CUPOSIT (registered trademark) COPPER MIX series, CIRCUPOSIT (registered trademark) series), electroless palladium plating solution (PALLAMERSE (registered trademark) series), electroless nickel plating solution (DURAPOSIT (registered trademark) series), electroless gold plating solution (AUROLECTROLESS (registered trademark) series), and electroless tin plating solution (TINPOSIT (registered trademark) series) manufactured by The Dow Chemical Company can be suitably used.

[0124] In the electroless plating process, plating bath-related factors including temperature, pH, immersion time, concentration of metal ion, the presence or absence of stirring and stirring speed, the presence or absence of feeding of air and oxygen and feeding speed may be adjusted to control the forming speed of a metal coating film and the thickness of the film.

Examples

[0125] The present invention will be described more specifically with reference to Examples, which are not intended to limit the present invention. In Examples, physical properties of the samples were measured by using the following apparatuses under the following conditions.

(1) GPC (Gel Permeation Chromatography)

Apparatus: HLC-8220GPC manufactured by Tosoh Corporation
Column: Shodex (registered trademark) KF-804L+KF-803L manufactured by Showa Denko K.K.
Column temperature: 40°C
Solvent: tetrahydrofuran
Detector: UV (254 nm), RI

(2) ^{1}H NMR spectra

Apparatus: JNM-L 400 manufactured by JEOL Ltd.
Solvent: $CDCl_3$
Internal reference: tetramethylsilane (0.00 ppm)

(3) ^{13}C NMR spectra

Apparatus: JNM-ECA700 manufactured by JEOL Ltd.
Solvent: $CDCl_3$
Relaxation reagent: chromium trisacetylacetonate ($Cr(acac)_3$)
Reference: $CDCl_3$ (77.0 ppm)

(4) ICP atomic emission spectroscopy (Inductively Coupled Plasma atomic emission spectroscopy)

Apparatus: ICPM-8500 manufactured by Shimadzu Corporation

(5) TEM (Transmission Electron Microscope) image

Apparatus: H-8000 manufactured by Hitachi High-Technologies Corporation

(6) UV-ozone cleaner

Apparatus: UV-208 manufactured by Technovision Inc.

(7) Electron microscope image

Apparatus: Digital Microscope VHX-2000 manufactured by Keyence Corporation

(8) Sectional SEM (Scanning Electron Microscope) image

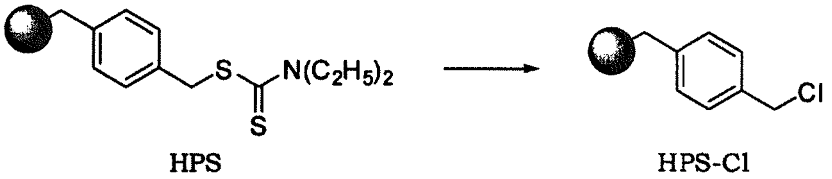
SEM: JSM-7400F manufactured by JEOL Ltd.
Sectional sample preparation apparatus: Cross Section Polisher (registered trademark) II IB-09020CP manufactured by JEOL Ltd.

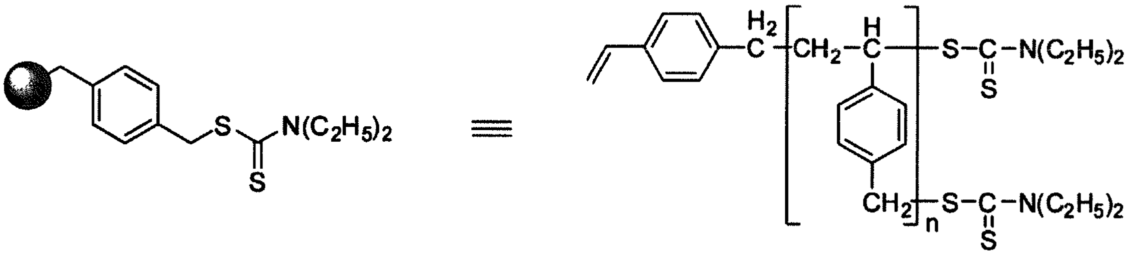
[0126] Abbreviations used are as follows:

HPS: hyperbranched polystyrene [HYPERTECH (registered trademark) HPS-200 manufactured by Nissan Chemical Industries, Ltd.]
AEAPM: 3-(2-aminoethylamino)propyl(dimethoxy)(methyl)silane [manufactured by Tokyo Chemical Industry Co., Ltd.]
AEAP: 3-(2-aminoethylamino)propyltrimethoxysilane [manufactured by Tokyo Chemical Industry Co., Ltd.]
APMES: 3-aminopropyl(diethoxy)(methyl)silane [manufactured by Tokyo Chemical Industry Co., Ltd.]
APES: 3-aminopropyltriethoxysilane [Shin-Etsu Silicone (registered trademark) KBE-903 manufactured by Shin-Etsu Chemical Co., Ltd.]
APMS: 3-aminopropyltrimethoxysilane [manufactured by Tokyo Chemical Industry Co., Ltd.]
BSPA: bis(3-trimethoxysilylpropyl)amine [manufactured by Tokyo Chemical Industry Co., Ltd.]
EMSO: epoxy group/methyl group containing methoxysilane oligomer [Shin-Etsu Silicone (registered trademark) X-41-1056 manufactured by Shin-Etsu Chemical Co., Ltd.]
GPMS: 3-(glycidyloxy)propyltrimethoxysilane [manufactured by Tokyo Chemical Industry Co., Ltd.]
PTMS: propyltrimethoxysilane [manufactured by Tokyo Chemical Industry Co., Ltd.]
F554: fluorine-based surfactant [Megafac (registered trademark) F-554 manufactured by DIC Corporation]
ITO: indium tin oxide
N6: nylon 6 substrate [UBE Nylon 102213 manufactured by Ube Industries, Ltd.]
N66: nylon 6,6 substrate [Reona (registered trademark) 1500 manufactured by Asahi Kasei Chemicals Corporation]
PEEK: polyetheretherketone film [Sumilite (registered trademark) FS-1100C manufactured by Sumitomo Bakelite Co., Ltd.]
PET: poly(ethylene terephthalate)
PET-1: poly(ethylene terephthalate) film [Lumirror (registered trademark) T60 manufactured by Toray Industries Inc.]
PET-2: easy adhesive poly(ethylene terephthalate) film [COSMOSHINE (registered trademark) A4100 manufactured by Toyobo Co., Ltd.]
PI: polyimide
PI-1: polyimide film [Kapton (registered trademark) 200EN manufactured by Du Pont-Toray Co., Ltd.]
PI-2: polyimide film [Upilex (registered trademark) 125S manufactured by Ube Industries, Ltd.]
IPA: isopropanol
IPE: diisopropyl ether
MEK: methyl ethyl ketone
THF: tetrahydrofuran

[Synthesis Example 1] Production of HPS-Cl

[0127]





[0128] A 500mL reaction flask was charged with 27 g of sulfuryl chloride [manufactured by KISHIDA CHEMICAL CO., LTD.] and 50 g of chloroform, and the mixture was stirred to be uniformly dissolved. This solution was cooled to 0°C under nitrogen stream.

[0129] Another 300mL reaction flask was charged with 15 g of a hyperbranched polymer HPS having a dithiocarbamate group at a molecular terminal and 150 g of chloroform, and the mixture was stirred under nitrogen stream until the mixture became uniform.

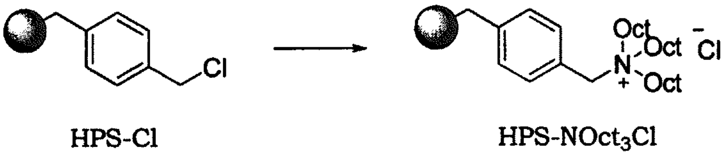
[0130] The HPS/chloroform solution was added with a feeding pump from the 300 mL reaction flask in which the HPS/ chloroform solution was placed to the sulfuryl chloride/ chloroform solution cooled to 0°C under nitrogen stream over 60 minutes so that the temperature of the reaction liquid was from -5 to 5°C. After the addition was completed, the reaction liquid was stirred for 6 hours while the temperature was kept at -5 to 5°C.

[0131] A solution in which 16 g of cyclohexene [manufactured by Tokyo Chemical Industry Co., Ltd.] was dissolved in 50 g of chloroform was added to this reaction liquid so that the temperature of the reaction liquid became from -5 to 5°C. After the addition was completed, this reaction liquid was added to 1,200 g of IPA to precipitate the polymer. This precipitate was filtered to obtain a white powder, which was dissolved in 100 g of chloroform. The liquid was added to 500 g of IPA to reprecipitate the polymer. This precipitate was filtered under reduced pressure and vacuum-dried to obtain 8.5 g of a hyperbranched polymer having a chlorine atom at a molecular terminal (HPS-Cl) as a white powder (yield 99%).

[0132] The ^{1}H NMR spectrum of the obtained HPS-Cl is shown in FIG. 1. Because the peaks derived from the dithiocarbamate group (4.0 ppm, 3.7 ppm) disappeared, it was found that almost all the dithiocarbamate groups at the molecular terminals of the HPS were replaced with chlorine atoms in the obtained HPS-Cl. The weight-average molecular weight Mw of the obtained HPS-Cl measured by GPC in terms of polystyrene was 14,000 and a degree of distribution Mw/Mn was 2.9.

[Synthesis Example 2] Production of HPS-$NOct_3Cl$

[0133]



[0134] A 100 mL reaction flask equipped with a condenser was charged with 4.6 g (30 mmol) of the HPS-Cl produced in Synthesis Example 1, 10.6 g (30 mmol) of trioctylamine [manufactured by JUNSEI CHEMICAL CO., LTD.], and 45 g of chloroform and was purged with nitrogen. The mixture was heated to reflux while stirring for 48 hours.

[0135] After the mixture was cooled to a liquid temperature of 30°C, the solvent was distilled off. The resultant residue was dissolved in 150 g of chloroform, and the solution was cooled to 0°C. The solution was added to 3,000 g of IPE at 0°C for purification by reprecipitation. The precipitated polymer was filtered under reduced pressure and vacuum-dried at 40°C to obtain 9.6 g of a hyperbranched polymer having a trioctylammonium group at a molecular terminal (HPS-$NOct_3Cl$) as a pale yellow powder.

[0136] The ^{13}C NMR spectrum of the obtained HPS-$NOct_3Cl$ is shown in FIG. 2. The peak of the methylene group bonded to the chlorine atom and the peak of the methylene group bonded to the ammonium group revealed that 71% of the chlorine atoms at the molecular terminals of the HPS-Cl were replaced with the ammonium groups in the obtained HPS-$NOct_3Cl$. The weight-average molecular weight Mw of the HPS-$NOct_3Cl$ calculated from the Mw (14,000) of the HPS-Cl and the degree of introduction (71%) of ammonium group was 37,000.

[Synthesis Example 3] Production of Pd[HPS-$NOct_3Cl$]

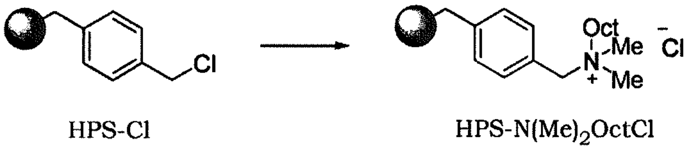
[0137] A 1 L two necked flask was charged with 4.3 g of palladium acetate [manufactured by Kawaken Fine Chemicals Co., Ltd.] and 200 g of chloroform, and the mixture was stirred until it became uniform. To this solution, a solution in which 18.0 g of HPS-$NOct_3Cl$ produced in Synthesis Example 2 was dissolved in 200 g of chloroform was added with a dropping funnel. The inside of the dropping funnel was washed out with 100 g of ethanol to the reaction flask. This mixture was stirred at 60°C for 17 hours.

[0138] After the mixture was cooled to a liquid temperature of 30°C, the solvent was distilled off. The resultant residue was dissolved in 300 g of THF, and the solution was cooled to 0°C. The solution was added to 6,000 g of IPE at 0°C for purification by reprecipitation. The precipitated polymer was filtered under reduced pressure and vacuum-dried at 60°C to obtain 19.9 g of a complex of the hyperbranched polymer having an ammonium group at a molecular terminal and Pd particles (Pd[HPS-$NOct_3Cl$]) as a black powder.

[0139] The result of ICP emission spectroscopy showed that the Pd content of the Pd[HPS-$NOct_3Cl$] was 11% by mass. The TEM (Transmission Electron Microscope) image showed that the Pd particles had a particle diameter of approximately 2 to 4 nm.

[Synthesis Example 4] Production of HPS-$N(Me)_2OctCl$

[0140]



[0141] A 100 mL reaction flask equipped with a condenser was charged with 4.6 g (30 mmol) of HPS-Cl produced in Synthesis Example 1 and 15 g of chloroform, and the mixture was stirred until it became uniform. To this solution, a solution in which 5.0 g (31.5 mmol) of dimethyl(octyl)amine [FARMIN (registered trademark) DM0898 manufactured by Kao Corporation] was dissolved in 7.5 g of chloroform was added, and 7.5 g of IPA was further added thereto. This mixture was stirred in a nitrogen atmosphere at 65°C for 40 hours.

[0142] After the mixture was cooled to a liquid temperature of 30°C, the solvent was distilled off. The resultant residue was dissolved in 60 g of chloroform, and the solution was added to 290 g of IPE for purification by reprecipitation. The precipitated polymer was filtered under reduced pressure and vacuum-dried at 50°C to obtain 9.3 g of a hyperbranched polymer having a dimethyloctylammonium group at a molecular terminal (HPS-$N(Me)_2OctCl$) as a white powder.

[0143] The ^{13}C NMR spectrum of the obtained HPS-$N(Me)_2OctCl$ is shown in FIG. 3. From the peak of the benzene ring and the peak of the methyl group of the octyl group at the terminal, it was found that, in the obtained HPS-$N(Me)_2OctCl$ the chlorine atoms at the molecular terminals of the HPS-Cl molecules were replaced with ammonium groups nearly quantitatively. The weight-average molecular weight of HPS-$N(Me)_2OctCl$ calculated from Mw (14,000) of HPS-Cl and the degree of introduction of ammonium group (100%) was 28,000.

[Synthesis Example 5] Production of Pd[HPS-$N(Me)_2OctCl$]

[0144] A 100 mL reaction flask equipped with a condenser was charged with 1.3 g of palladium acetate [manufactured by Kawaken Fine Chemicals Co., Ltd.] and 23 g of chloroform, and the mixture was stirred until it became uniform. To this solution, a solution in which 0.4 g ofHPS-$N(Me)_2OctCl$ produced in Synthesis Example 4 was dissolved in 23 g of chloroform was added with a dropping funnel. The inside of the dropping funnel was washed with 23 g of chloroform and 23 g of ethanol and the chloroform and ethanol were added to the reaction flask. This mixture was stirred in a nitrogen atmosphere at 65°C for 8 hours.

[0145] After the mixture was cooled to a liquid temperature of 30°C, the solvent was distilled off. The resultant residue was dissolved in 10 g of chloroform, and the solution was added to 100 g of IPE for purification by reprecipitation. The precipitated polymer was filtered under reduced pressure and vacuum-dried at 60°C to obtain, as a black powder, 1.0 g of a complex of the hyperbranched polymer having an ammonium group at a molecular terminal and Pd particles (Pd[HPS-$N(Me)_2OctCl$]).

[0146] The result of ICP emission spectroscopy showed that the Pd content of the Pd[HPS-$N(Me)_2OctCl$ was 61% by mass. The TEM (Transmission Electron Microscepe) image showed that the Pd particles had a particle diameter of approximately 2 to 5 nm.

[Reference Example 1] Preparation of electroless nickel plating solution

[0147] AIL flask was charged with 50 mL of Melplate (registered trademark) NI-6522LF1 [manufactured by Meltex Inc.], 150 mL of Melplate (registered trademark) NI-6522LF2 [manufactured by Meltex Inc.], and 5 mL of Melplate (registered trademark) NI-6522LF Additive [manufactured by Meltex Inc.], and pure water was added to make a total volume of 1 L of solution. To this solution, a 10 vol% sulphuric acid aqueous solution was added to adjust the pH of the solution to 4.6 to obtain the electroless nickel plating solution.

[Reference Example 2] Preparation of electroless copper plating solution

[0148] A 100 mL flask was charged with 47 mL of pure water, 25 mL of CUPOSIT (registered trademark) COPPER MIX 328A [manufactured by Dow Chemical], 25 mL of CUPOSIT (registered trademark) COPPER MIX 328L [manufactured by Dow Chemical], and 3 mL of CUPOSIT (registered trademark) COPPER MIX 328C [manufactured by Dow Chemical] in order, and the mixture was stirred to form an electroless copper plating solution.

[Examples 1 to 4 and Comparative Examples 1 and 2] Electroless plating on glass substrate

[0149] 20 mg of Pd[HPS-$NOct_3Cl$] produced in Synthesis Example 3 and 100 mg of each of the alkoxysilanes listed in Table 1 were dissolved in 2.55 g of n-propanol to prepare a primer for electroless plating with a solid content of 4.5% by mass.

[0150] The primer was spin-coated (200 rpm × 5 seconds and then 1,000 rpm x 30 seconds) on a glass substrate (50 mm × 50 mm). This substrate was dried on a hot plate at 80°C for 5 minutes to obtain a glass substrate having a priming layer on the whole surface of the substrate.

[0151] The obtained substrate was immersed in the electroless nickel plating solution prepared in Reference Example 1 heated to 75°C for 180 seconds. The substrate taken out therefrom was washed with water and was dried on a hot plate at 80°C for 5 minutes to obtain a plated substrate.

[0152] For the metal plating films on the respective plated substrates obtained in Examples 1 to 4 and Comparative Examples 1 and 2, film uniformity and substrate adhesion were evaluated.

[0153] The film uniformity was visually evaluated in accordance with the following criteria. For the substrate adhesion, a piece of 18 mm-wide CELLOTAPE (registered trademark) [manufactured by Nichiban Co., Ltd. CT-18S] was applied to the obtained metal plating film area on the plated substrate and was strongly rubbed against the substrate with a finger to securely adhere. The adhered CELLOTAPE (registered trademark) was then peeled off at one go, and the state of the metal plating film was visually evaluated in accordance with the following criteria. Table 1 collectively lists the results.

<Evaluation of film uniformity>

[0154]

A: A metal plating film having metallic luster is precipitated without non-uniformity on the whole surface of a substrate on which a priming layer is formed.
B: Although the surface of a substrate is covered, there is non-uniformity in luster.
C: A substrate has some exposed parts and is not perfectly covered.

<Evaluation of substrate adhesion>

[0155]

A: A metal plating film is not separated and adheres to a substrate.
B: A metal plating film is partially separated.
C: Most (approximately 50% or more) of a metal plating film is separated and attached to CELLOTAPE (registered trademark).

Table 1

	Alkoxysilane	Film uniformity	Substrate adhesion
Example 1	APMS	A	A

(continued)

	Alkoxysilane	Film uniformity	Substrate adhesion
Example 2	APES	A	A
Example 3	AEAP	A	A
Example 4	BSPA	A	A
Comparative Example 1	Not Added	B	C
Comparative Example 2	PTMS	B	C

[0156] As listed in Table 1, when forming the plating films using the primer of the present invention comprising the alkoxysilane having an amino group (Examples 1 to 4), the formed metal plating films had excellent uniformity and had adhesion in terms of the tape test.

[0157] In contrast, the metal plating film formed using the primer containing no alkoxysilane (Comparative Example 1) and the metal plating film formed on the primer comprising the alkoxysilane having no amino group (Comparative Example 2) had low uniformity and had no adhesion.

[0158] The above results reveal that the primer for plating comprising the alkoxysilane having an amino group of the present invention is advantageous in obtaining a plating film having uniformity and high adhesion.

[Examples 5 to 8 and Comparative Examples 3 and 4] Electroless plating on ITO film on glass

[0159] 20 mg of Pd[HPS-NOct$_3$Cl] produced in Synthesis Example 3 and 100 mg of each of the alkoxysilanes listed in Table 2 were dissolved in 2.55 g of n-propanol to prepare a primer for electroless plating with a solid content of 4.5% by mass.

[0160] The primer was spin-coated (200 rpm x 5 seconds and then 1,000 rpm x 30 seconds) on each of the ITO films on the glass substrates with an ITO film (50 mm x 50 mm) [manufactured by foresight Co., Ltd]. This substrate was dried on a hot plate at 80°C for 5 minutes to obtain a glass substrate with the ITO film having a priming layer on the whole surface of the ITO film.

[0161] The obtained substrate was immersed for 180 seconds in the electroless nickel plating solution prepared in Reference Example 1 heated to 75°C. The substrate taken out therefrom was washed with water and was dried on a hot plate at 80°C for 5 minutes to obtain a plated substrate.

[0162] For the metal plating films on the respective plated substrates obtained in Examples 5 to 8 and Comparative Examples 3 and 4, film uniformity and ITO film adhesion were evaluated by the above methods. Table 2 collectively lists the results. The following criteria are used for evaluation.

<Evaluation of film uniformity>

[0163]

A: A metal plating film having metallic luster is precipitated on the whole surface of an ITO film on which a priming layer is formed without non-uniformity.
B: Although the surface of an ITO film is covered, there is non-uniformity in luster.
C: An ITO film has some exposed parts and is not perfectly covered.

<Evaluation of ITO film adhesion>

[0164]

A: A metal plating film is not separated and adheres to an ITO film.
B: A metal plating film is partially separated.
C: Most (approximately 50% or more) of a metal plating film is separated and adheres to CELLOTAPE (registered trademark).

Table 2

	Alkoxysilane	Film uniformity	ITO film adhesion
Example 5	APMS	A	A
Example 6	APES	A	A
Example 7	AEAP	A	A
Example 8	BSPA	A	A
Comparative Example 3	Not Added	B	C
Comparative Example 4	PTMS	B	C

[0165] As listed in Table 2, when the plating films were formed using the primer of the present invention comprising the alkoxysilane having an amino group (Examples 5 to 8), the formed metal plating films had excellent uniformity and had adhesion in terms of the tape test.

[0166] In contrast, the metal plating film formed using the primer containing no alkoxysilane (Comparative Example 3) and the metal plating film formed on the primer comprising the alkoxysilane having no amino group (Comparative Example 4) had low uniformity and had no adhesion.

[0167] The above results reveal that the primer for plating comprising the alkoxysilane having an amino group of the present invention is advantageous in obtaining a plating film having uniformity and high adhesion also for the ITO films on glass.

[Examples 9 to 13 and Comparative Examples 5 and 6] Electroless plating on PI film

[0168] 20 mg of Pd[HPS-NOct$_3$Cl] produced in Synthesis Example 3 and 100 mg of each of the alkoxysilanes listed in Table 3 were dissolved in 2.55 g of n-propanol to prepare a primer for electroless plating with a solid content of 4.5% by mass.

[0169] The primer was spin-coated (200 rpm x 5 seconds and then 1,000 rpm x 30 seconds) on each of the PI films (50 mm × 50 mm) listed in Table 3. This film was dried on a hot plate at 80°C for 5 minutes to obtain a PI film having a priming layer on the whole surface of the film.

[0170] The obtained film was immersed in the electroless nickel plating solution prepared in Reference Example 1 heated to 75°C for 180 seconds. The film taken out therefrom was washed with water and was dried on a hot plate at 80°C for 5 minutes to obtain a plated film.

[Examples 23 to 25] Electroless plating on PI film

[0171] The procedure in Example 9 was repeated to obtain a plated film except that the drying conditions after the primer application and after the washing with water were 150°C and 10 minutes respectively, and that the bath temperature of the electroless nickel plating solution was changed to 80°C.

[0172] For the metal plating films on the respective plated films obtained in Examples 9 to 13 and 23 to 25 and Comparative Examples 5 and 6, film uniformity and film adhesion were evaluated by the above methods. Table 3 collectively lists the results. The following criteria are used for evaluation.

<Evaluation of film uniformity>

[0173]

A: A metal plating film having metallic luster is precipitated on the whole surface of a film on which a priming layer is formed without non-uniformity.
B: Although the surface of a film is covered, there is non-uniformity in luster.
C: A film has some exposed parts and is not perfectly covered.

<Evaluation of film adhesion>

[0174]

A: A metal plating film is not separated and adheres to a film.

B: A metal plating film is partially separated.

C: Most (approximately 50% or more) of a metal plating film is separated and adheres to CELLOTAPE (registered trademark).

Table 3

	Alkoxysilane	PI film	Film uniformity	Film adhesion
Example 9	APMS	PI-1	A	A
Example 10	APMS	PI-2	A	A
Example 11	APES	PI-1	A	B
Example 12	AEAP	PI-1	A	A
Example 13	BSPA	PI-1	A	B
Example 23	APMES	PI-1	A	A
Example 24	AEAP	PI-1	A	A
Example 25	AEAPM	PI-1	A	A
Comparative Example 5	Not Added	PI-1	A	C
Comparative Example 6	PTMS	PI-1	A	C

[0175] As listed in Table 3, when the plating films were formed using the primer of the present invention comprising the alkoxysilane having an amino group (Examples 9 to 13 and 23 to 25), the formed metal plating films had excellent uniformity and had adhesion in terms of the tape test. For the different kind of PI film, a similar effect was revealed (Example 10).

[0176] In contrast, the metal plating film formed using the primer containing no alkoxysilane (Comparative Example 5) and the metal plating film formed on the primer comprising the alkoxysilane having no amino group (Comparative Example 6) had excellent uniformity but had no adhesion.

[0177] The above results reveal that the primer for plating comprising the alkoxysilane having an amino group of the present invention is advantageous in obtaining a plating film having uniformity and high adhesion also for the PI films.

[Example 14 and Comparative Examples 7 and 8] Electroless plating on nylon 6,6 substrate-1

[0178] 100 mg of Pd[HPS-NOct$_3$Cl] produced in Synthesis Example 3, 10 mg of each of the alkoxysilanes listed in Table 4, and 1 mg of fluorine-based surfactant F554 were dissolved in 39.89 g of IPA to prepare a primer for electroless plating with a solid content of 0.28% by mass.

[0179] The primer was dip-coated on a nylon substrate N66 (10 × 50 × 1 mm) whose surface had been hydrophilized by being immersed in a 40°C, 8% by mass hydrochloric acid for 10 minutes. This substrate was dried in a drier at 80°C for 10 minutes to obtain a nylon substrate having a priming layer on the whole surface of the substrate.

[0180] The obtained substrate was immersed in the electroless nickel plating solution prepared in Reference Example 1 heated to 70°C for 180 seconds. The substrate taken out therefrom was washed with water and was dried in a drier at 80°C for 10 minutes to obtain a plated substrate.

[Example 15] Electroless plating on nylon 6,6 substrate-2

[0181] 50 mg of Pd[HPS-NOct$_3$Cl] produced in Synthesis Example 3 and 5 mg of EMSO as an alkoxysilane were dissolved in 7.95 g of IPA to prepare a primer for electroless plating with a solid content of 0.69% by mass.

[0182] The procedure in Example 14 was repeated to obtain a plated substrate except that the above primer was used.

[Example 16] Electroless plating on nylon 6 substrate

[0183] The procedure in Example 15 was repeated to obtain a plated substrate except that IPA and the nylon substrate were changed to MEK and N6, respectively.

For the metal plating films on the respective plated substrates obtained in Examples 14 to 16, film uniformity and substrate adhesion were evaluated by the above methods. Table 4 collectively lists the results. The same criteria as those for Examples 1 to 4 and Comparative Examples 1 and 2 were used.

[0184]

Table 4

	Alkoxysilane	Nylon substrate	Film uniformity	Substrate adhesion
Example 14	GPMS	N66	A	A
Example 15	EMS	N66	A	A
Example 16	EMSO	N6	A	A
Comparative Example 7	Not Added	N66	B	C
Comparative Example 8	PTMS	N66	B	C

[0185] As listed in Table 4, when forming the plating films using the primer of the present invention comprising the alkoxysilane having an epoxy group (Examples 14 to 16), the formed metal plating films had excellent uniformity and had adhesion in terms of the tape test. For the different kind of nylon substrate, a similar effect was revealed (Example 16).

[0186] In contrast, the metal plating film formed using the primer containing no alkoxysilane (Comparative Example 7) and the metal plating film formed on the primer comprising the alkoxysilane having no epoxy group (Comparative Example 8) had low uniformity and had no adhesion.

[0187] The above results reveal that the primer for plating comprising the alkoxysilane having an epoxy group of the present invention is advantageous in obtaining a plating film having uniformity and high adhesion.

[Example 17] Electroless plating on PEEK film

[0188] 20 mg of Pd[HPS-NOct$_3$Cl] produced in Synthesis Example 3 and 100 mg of APMS were dissolved in 2.55 g of n-propanol to prepare a primer for electroless plating with a solid content of 4.5% by mass.

[0189] The primer was spin-coated (200 rpm x 5 seconds and then 1,000 rpm x 30 seconds) on a PEEK film (30 mm x 30 mm) whose surface had been hydrophilized using a UV ozone cleaning apparatus beforehand. This film was dried on a hot plate at 80°C for 10 minutes to obtain a PEEK film having a priming layer on the whole surface of the film.

[0190] The obtained film was immersed in the electroless nickel plating solution prepared in Reference Example 1 heated to 75°C for 180 seconds. The film taken out therefrom was washed with water and was dried on a hot plate at 80°C for 10 minutes to obtain a plated film.

[Example 18] Electroless plating on PET film-1

[0191] The procedure in Example 17 was repeated to obtain a plated film except that the PEEK film was changed to PET-1 (40 mm x 40 mm) whose surface had been hydrophilized using a UV ozone cleaning apparatus beforehand.

[Example 19] Electroless plating on PET film-2

[0192] The procedure in Example 17 was repeated to obtain a plated film except that the PEEK film was changed to PET-2 (40 mm x 40 mm).

[0193] For the metal plating films on the respective plated films obtained in Examples 17 to 19, film uniformity and substrate adhesion were evaluated by the above methods. Table 5 collectively lists the results. The same criteria as those for Examples 9 to 13 and Comparative Examples 5 and 6 were used.

Table 5

	Film	Film uniformity	Film adhesion
Example 17	PEEK	A	A
Example 18	PET-1	A	A
Example 19	PET-2	A	A

[0194] As listed in Table 5, the plating films formed using the primer of the present invention comprising the alkoxysilane having an amino group had excellent uniformity and had adhesion in terms of the tape test for all the films.

[Example 20] Electroless plating on PI film-2

[0195] 1.0 g of Pd[HPS-NOct$_3$Cl] produced in Synthesis Example 3 and 4.0 g of APMS were dissolved in 95 g of a butylcellosolve/n-hexanol mixed solution (mass ratio 4:1) to prepare a primer for electroless plating with a solid content of 5% by mass.

[0196] Using a fine droplet ejecting apparatus filled with the primer, inkjet coating was performed on the PI film PI-1. Specifically, using the fine droplet ejecting apparatus having 85 droplet ejecting nozzles in a row at intervals of 423 μm, the primer was ejected onto the PI film 571 times per second while moving the fine droplet ejecting apparatus by 10 cm at 40 mm/second relatively while keeping a gap of 0.5 mm relative to the PI film. In other words, it is estimated that the primer is applied onto the PI film at intervals of 423 μm in an X-axial direction (the direction in which the nozzles are arranged) and at intervals of 70 μm in a Y-axial direction (the travel direction of the fine droplet ejecting apparatus). The amount of liquid of the primer per droplet calculated from an obtained film thickness was approximately 20 to 40 pL.

[0197] The film to which the primer had been applied was left as it was (approximately 25°C) for 1 minute and was dried on a hot plate at 160°C for 5 minutes to obtain a PI film having 85 linear priming layers on the film.

[0198] The obtained film was immersed for 300 seconds in the electroless nickel plating solution prepared in Reference Example 1 heated to 90°C. The film taken out therefrom was washed with water and was dried on a hot plate at 100°C for 5 minutes to obtain a plated film. FIG. 4 shows an electron microscope image of the obtained metal plating film on the film, whereas FIG. 5 shows a sectional SEM image of one linear metal plating film.

[0199] The obtained metal plating film on the film was observed to find that the metal plating film having metallic luster was precipitated on the whole surface of the priming layers formed linearly without non-uniformity and the metal plating film was uniformly formed. The film adhesion of the metal plating film was evaluated by the above method to find that the metal plating film was not separated and remained adhering to the film regardless of whether the direction of peeling off CELLOTAPE (registered trademark) was the X-axial direction or the Y-axial direction.

[Example 21] Electroless plating on PI film-3

[0200] 20 mg of Pd[HPS-N(Me)$_2$OctCl] produced in Synthesis Example 5 and 20 mg of APMS were dissolved in 1.96 g of ethanol to prepare a primer for electroless plating with a solid content of 2% by mass.

[0201] A solution obtained by further diluting the primer six times with ethanol was spin-coated (200 rpm x 5 seconds and then 1,000 rpm x 30 seconds) on the PI film PI-1 (40 mm x 40 mm) whose surface had been hydrophilized using a UV ozone cleaning apparatus beforehand. This film was dried on a hot plate at 150°C for 5 minutes to obtain a PI film having a priming layer on the whole surface of the film.

[0202] The obtained film was immersed for 180 seconds in the electroless nickel plating solution prepared in Reference Example 1 heated to 75°C. The film taken out therefrom was washed with water and was dried on a hot plate at 150°C for 5 minutes to obtain a plated film.

[0203] For the obtained metal plating film on the plated film, film uniformity and film adhesion were evaluated by the above methods, and both of the evaluation results were A.

[Example 22] Electroless copper plating on PI film

[0204] A PI film having a priming layer on the whole surface of the film produced by the same method as Example 21 was immersed for 300 seconds in the electroless copper plating solution prepared in Reference Example 2 temperature-regulated at 25°C. The film taken out therefrom was washed with water and was dried on a hot plate at 150°C for 5 minutes to obtain a plated film.

[0205] For the metal plating film on the plated film, film uniformity and film adhesion were evaluated by the above methods, and both of the evaluation results were A.

Prior Art Document

Patent Document

[0206] Patent Document 1: WO 2010/021386 Pamphlet

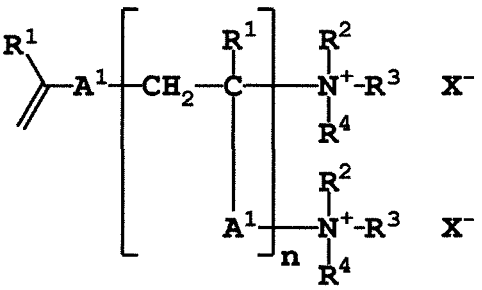
Claims

1. A primer for forming a metal plating film on a base material by electroless plating, the primer comprising:

   (a) a hyperbranched polymer having an ammonium group at a molecular terminal and a weight-average molecular weight of 500 to 5,000,000;
   (b) a metal fine particle; and
   (c) an alkoxysilane having an amino group optionally substituted with an aliphatic group or an epoxy group, or an oligomer of the alkoxysilane.

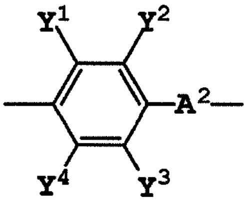
2. The primer according to claim 1, wherein
   the ammonium group of the hyperbranched polymer (a) is attached to the metal fine particle (b) to form a complex.

3. The primer according to claim 1 or 2, wherein
   the hyperbranched polymer (a) is a hyperbranched polymer of Formula [1]:



[1]

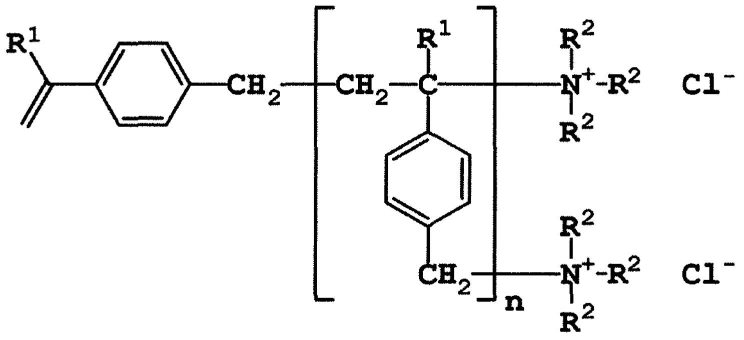
(where R^1 are each independently a hydrogen atom or a methyl group; R^2 to R^4 are each independently a hydrogen atom, a linear, branched, or cyclic alkyl group having a carbon atom number of 1 to 20, a C_{7-20} arylalkyl group, or $-(CH_2CH_2O)_mR^5$ (where R^5 is a hydrogen atom or a methyl group; and m is an integer of 2 to 100) (where the alkyl group and the arylalkyl group are optionally substituted with an alkoxy group, a hydroxy group, an ammonium group, a carboxy group, or a cyano group), or two groups of R^2 to R^4 together represent a linear, branched, or cyclic alkylene group, or R^2 to R^4 together with a nitrogen atom to which R^2 to R^4 are bonded optionally form a ring; X^- is an anion; n is the number of repeating unit structures and an integer of 5 to 100,000; and A^1 is a structure of Formula [2]:



[2]

(where A^2 is a linear, branched, or cyclic alkylene group having a carbon atom number of 1 to 30 optionally containing an ether bond or an ester bond; and Y^1 to Y^4 are each independently a hydrogen atom, a C_{1-20} alkyl group, a C_{1-20} alkoxy group, a nitro group, a hydroxy group, an amino group, a carboxy group, or a cyano group)).

4. The primer according to claim 3, wherein
   the hyperbranched polymer (a) is a hyperbranched polymer of Formula [3]:



[3]

(where R^1, R^2, and n have the same meanings as described above).

5. The primer according to any one of claims 1 to 4, wherein
the metal fine particle (b) is a fine particle of at least one selected from the group consisting of iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), palladium (Pd), silver (Ag), tin (Sn), platinum (Pt), and gold (Au).

6. The primer according to claim 5, wherein
the metal fine particle (b) is a palladium fine particle.

7. The primer according to claim 5 or 6, wherein
the metal fine particle (b) is a fine particle having an average particle diameter of 1 to 100 nm.

8. The primer according to any one of claims 1 to 7, wherein
the alkoxysilane (c) is a compound of Formula [4]:

$$\text{Z-L-Si}(R^6)_a(OR^7)_{3-a} \qquad [4]$$

(where R^6 is a C_{1-6} alkyl group or a phenyl group; R^7 are each independently a methyl group or an ethyl group; L is a C_{1-6} alkylene group optionally containing an ether bond; Z is an amino group optionally substituted with an aliphatic group, or an epoxy group; and a is 0 or 1).

9. A priming layer for electroless plating, obtained by forming a layer of the primer as claimed in any one of claims 1 to 8.

10. A metal plating film, formed on the priming layer by performing electroless plating on the priming layer for electroless plating as claimed in claim 9.

11. A metal-coated base material comprising:

    a base material;
    the priming layer for electroless plating as claimed in claim 9 formed on the base material; and
    the metal plating film as claimed in claim 10 formed on the priming layer for electroless plating.

12. A method for producing a metal-coated base material, the method comprising:

    a process A: coating a base material with the primer as claimed in any one of claims 1 to 8 to form a priming layer; and
    a process B: immersing the base material having the priming layer in an electroless plating bath to form a metal plating film.

Fig. 1

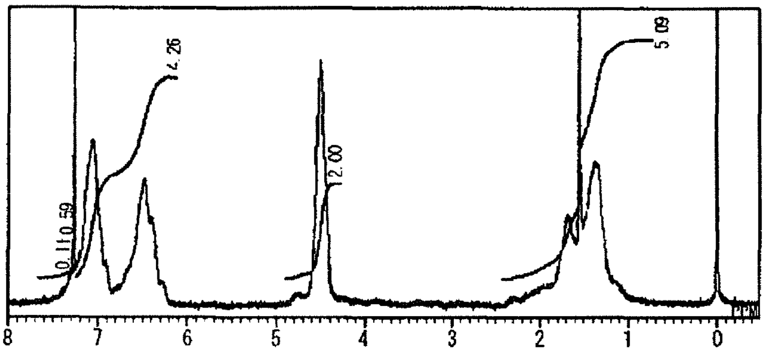


Fig. 2

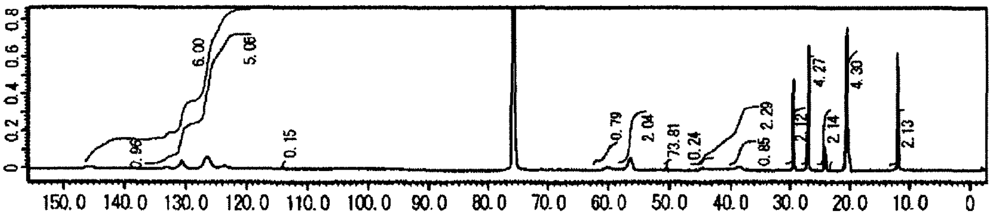


Fig. 3

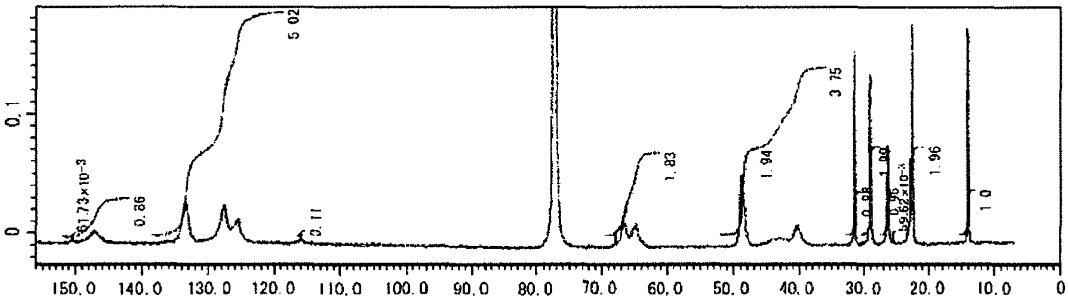


Fig. 4

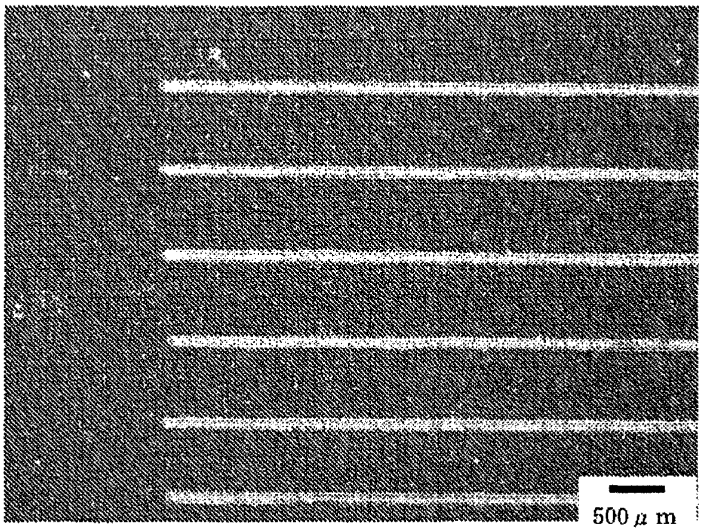
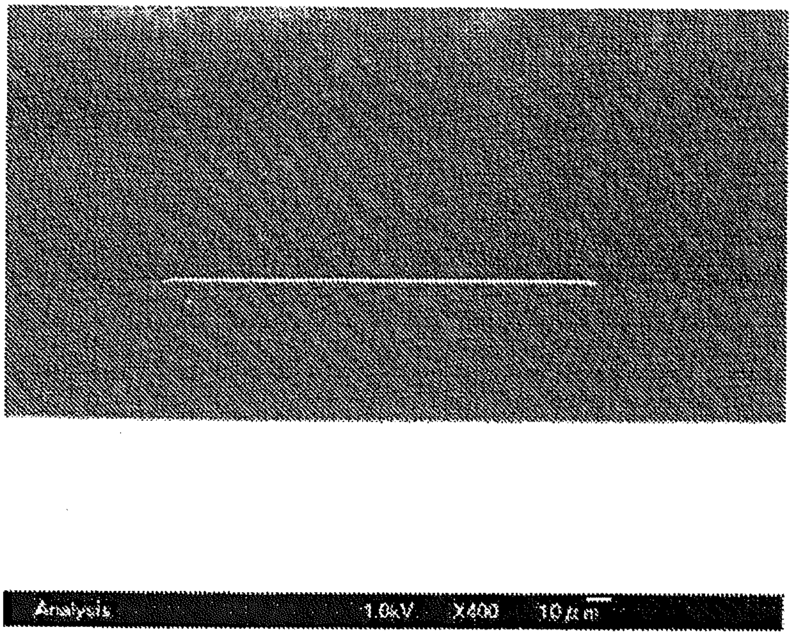


Fig 5



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/074714

A. CLASSIFICATION OF SUBJECT MATTER
C23C18/30(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)
C23C18/30

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2013
Kokai Jitsuyo Shinan Koho	1971-2013	Toroku Jitsuyo Shinan Koho	1994-2013

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.
Y	JP 2008-7849 A (Nippon Paint Co., Ltd.), 17 January 2008 (17.01.2008), entire text (Family: none)	1-12
Y	WO 2010/021386 A1 (Nissan Chemical Industries, Ltd.), 25 February 2010 (25.02.2010), entire text & US 2011/0183837 A1 & EP 2332640 A1 & CN 102131573 A & KR 10-2011-0073462 A & TW 201016723 A	1-12

☐ 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 27 September, 2013 (27.09.13)	Date of mailing of the international search report 08 October, 2013 (08.10.13)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 2008029688 A **[0049]**
- WO 2010021386 A **[0206]**

Non-patent literature cited in the description

- *Journal of Organometallic Chemistry,* 1996, vol. 520, 143-162 **[0084]**