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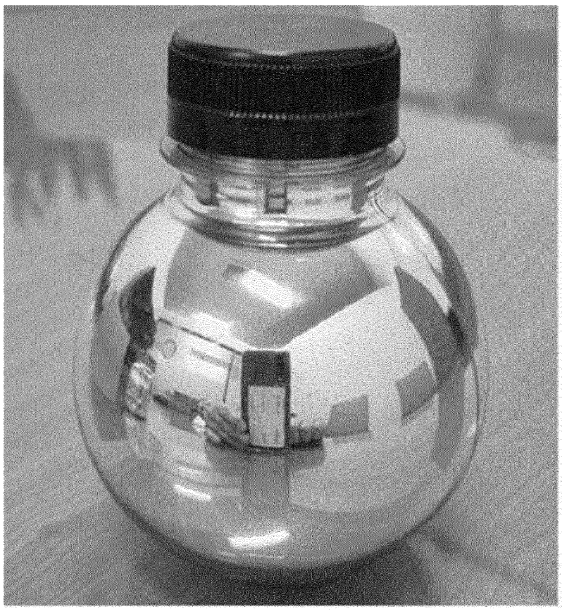
(54) SILVER PLATING SOLUTION

(57) An electroless silver plating solution is provided. The electroless silver plating solution includes a silver complex solution and a reducing agent solution. The silver complex solution includes a silver carboxylate represented by Formula 1: R_1-COOAg, a nitrogen-containing compound as a complexing agent, and a solvent. The reducing agent solution includes a reducing agent selected from the group consisting of glucose, hydrazine, hydroquinone, and derivatives thereof and a solvent. The electroless silver plating is based on a silver mirror reaction between the silver complex solution and the reducing agent solution.

[Fig. 3]



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Description

Technical Field

[0001] The present invention relates to a silver plating solution that can be used to manufacture a high-quality silver-plated product in an environmentally friendly and simple manner, and a silver-plated product manufactured using the silver plating solution.

Background Art

[0002] Silver belongs to the category of precious metals and has been used as a material for high-end ornaments, tableware, and coins from ancient times. In recent years, silver has been used in a wide variety of applications, for example, cellular phones, batteries (including solar cells), automobiles, electrodes of electronic devices such as semiconductors, electromagnetic wave shielding and heat dissipating products, and mechanical parts due to its excellent electrical, thermal, optical, and frictional properties and high antibacterial activity compared to other metals. Silver has also been widely applied to catalysts for electrochemical reactions and medical and antibacterial products. In addition, mirrors for general household use or high-end metal gloss products with high reflectance are manufactured by painting, plating or deposition with highly reflective metals such as silver, aluminum, chrome, nickel, titanium, and copper. Painting, coating, and printing are generally used in the manufacture of products whose conductivity or reflectance is not very high. Plating can be used to provide highly conductive and reflective films and even thin films with high-quality surface gloss but may increase the number of defects in the products, incur considerable costs, and discharge harmful substances, causing air pollution and wastewater problems. Vacuum deposition and sputtering are dry processes that enable the manufacture of thin-film electrodes or highly reflective films. However, deposition processes require the use of expensive vacuum equipment and limit the shape or size of substrates. Further, deposition processes are suitable for small quantity batch production, causing problems in the manufacture of products on a large scale. As such, plating processes cannot be applied to the manufacture of desired industrial electrical and electronic products or household products and have many environmental problems such as wastewater treatment problems that need to be solved.

[0003] Silver plating is largely divided into silver electroplating and electroless silver plating. Both silver plating processes share the use of a silver precursor or complex in common, but electroless silver plating is distinguished from silver electroplating in that it uses a reducing agent to deposit silver instead of using electricity and facilitates plating of electrically non-conductive plastic, fiber, and ceramic products. In particular, silver electroplating has long been performed in alkaline cyanide solutions (for example, potassium cyanide and sodium cyanide solutions) containing highly toxic silver cyanide. A lot of research and development has been conducted over the past decades to replace silver plating using a cyanide compound with cyanide-free silver plating using a silver compound such as silver nitrate and various complexing agents and other additives. However, silver plating using a cyanide compound is still used as a major process for the manufacture of commercial products because cyanide-free silver plating is disadvantageous in terms of adhesion, has difficulty in manufacturing bright silver-plated products, and has the disadvantage that the plating solution is vulnerable to contamination. As examples of cyanide-free silver plating, U.S. Patent No. 5,322,553 discloses the use of silver thiosulfate or silver sulfite to provide a more stable plating solution, U.S. Patent No. 6,620,304 mentions the possibility of manufacturing high-quality products using a plating solution that contains silver methanesulfonate and an amino acid such as cysteine without the need for any harmful substances, and U.S. Patent No. 8,608,932 discloses a differentiated silver electroplating method using a silver complex of 5,5-dimethylhydantoin. However, a plating solution whose price and quality are comparable to those of cyanide-containing plating solutions has not yet been developed. From an environmental point of view, the development of a silver plating solution without a cyanide compound remains an ongoing task. A silver ammonium complex, called Tollens' reagent, is reduced to form a silver mirror upon reaction with a compound having an aldehyde group, such as glucose. This is a kind of electroless silver plating that clearly shows a redox reaction and is used in the manufacture of vacuum flasks or Dewar bottles. However, since the silver plating solution is prepared from a strongly alkaline aqueous solution using silver nitrate and aqueous ammonia as a complexing agent, silver nitride is formed during storage, posing the risk of explosion. For this reason, the silver plating solution should be used immediately after its preparation and subjected to acid treatment without being stored after use for disposal. A plating solution using silver nitrate and aqueous ammonia as a complexing agent is excellent in stability during silver electroplating or electroless silver plating and quality, but its use is extremely limited due to the problems described above. Thus, the choice of a suitable type of complexing agent and a corresponding suitable reducing agent becomes a very important factor for electroless silver plating.

[0004] Under these circumstances, the present inventors have continued their effort to solve the problems encountered during silver plating and finally arrived at the present invention.

Detailed Description of the Invention

Problems to be Solved by the Invention

[0005] An object of the present invention is to provide an environmentally friendly and highly stable silver plating solution and a high-quality silver-plated product manufactured using the silver plating solution.

Means for Solving the Problems

[0006] According to one aspect of the present invention, there is provided an electroless silver plating solution including a silver complex solution and a reducing agent solution wherein the silver complex solution includes a silver carboxylate represented by Formula 1:

[Formula 1] R_1-COOAg

wherein R_1 is hydrogen, substituted or unsubstituted C_1-C_{22} alkyl, substituted or unsubstituted C_3-C_{30} cycloalkyl, substituted or unsubstituted C_6-C_{30} aralkyl, substituted or unsubstituted C_1-C_{30} heteroalkyl, substituted or unsubstituted C_2-C_{30} heterocycloalkyl or substituted or unsubstituted C_5-C_{30} heteroaralkyl, and the electroless silver plating is based on a silver mirror reaction between the silver complex solution and the reducing agent solution.

[0007] According to another aspect of the present invention, there is provided a silver-plated product manufactured by reaction with the silver plating solution at 5 to 50 °C.

Effects of the Invention

[0008] The silver plating solution of the present invention is environmentally friendly and is excellent in storage stability and performance. Due to these advantages, the silver plating solution of the present invention can be used to provide various high-quality silver-plated products.

Brief Description of the Drawings

[0009]

Fig. 1 is a photograph showing silver mirrors products manufactured in Examples 1-7.
Fig. 2 is a photograph showing a glass bottle manufactured in Example 3 as a silver mirror product.
Fig. 3 is a photograph showing a PET bottle manufactured in Example 8 as a silver mirror product.
Fig. 4 is a photograph showing a silver-plated nylon fabric product manufactured in Example 41 and the conductivity of the product.
Fig. 5 is a photograph showing a silver-plated nylon fiber product manufactured in Example 42 and the conductivity of the product.
Fig. 6 is a surface scanning electron microscopy (SEM) image of a silver-plated nylon fiber product manufactured in Example 42.
Fig. 7 is a photograph showing a silver-plated mirror-like polyimide film manufactured in Example 43.
Fig. 8 is a photograph showing a silver-plated polyurethane foam manufactured in Example 45.
Fig. 9 is a surface scanning electron microscopy (SEM) image of a silver-plated polyurethane foam manufactured in Example 45.
Fig. 10 is a photograph showing a silver-plated copper foil manufactured in Example 50.
Fig. 11 is a photograph showing a silver-containing antibacterial cotton fabric manufactured in Example 51.
Fig. 12 is a photograph showing the state of a silver complex solution prepared in Preparative Example 2 after storage at room temperature for 6 months.
Fig. 13 is a photograph showing the state of a reducing agent solution prepared in Preparative Example 8 after storage at room temperature for 6 months.

Brief Description of the Drawings

[0010] As used herein, the term "alkyl" includes straight, branched, cyclic hydrocarbon radicals, and combinations thereof. The term may optionally include one or more double bonds, triple bonds or a combination thereof in the chain. That is, "alkyl" is intended to include alkenyl and alkynyl.

[0011] The term "heteroalkyl", by itself or in combination with another term, means, unless otherwise stated, a stable

straight, branched, cyclic hydrocarbon radical or a combination thereof, consisting of one or more carbon atoms and one or more heteroatoms selected from the group consisting of O, N, P, Si, and S, and wherein the nitrogen, phosphorus, and sulfur atoms may optionally be oxidized and the nitrogen heteroatom may optionally be quaternized.

[0012] The terms "cycloalkyl" and "heterocycloalkyl", by themselves or in combination with other terms, represent, unless otherwise stated, cyclic versions of "alkyl" and "heteroalkyl", respectively.

[0013] The term "aryl" means, unless otherwise stated, a polyunsaturated, aromatic, hydrocarbon substituent which can be a single ring or multiple rings (from 1 to 3 rings) which are fused together or linked covalently.

[0014] The term "heteroaryl" refers to aryl groups (or rings) that contain from one to four heteroatoms (in each separate ring in the case of multiple rings) selected from N, O, and S, wherein the nitrogen and sulfur atoms are optionally oxidized, and the nitrogen atom(s) are optionally quaternized. The heteroaryl group can be attached to the remainder of the molecule through a carbon or heteroatom.

[0015] The term "aralkyl" refers to an alkyl group substituted with an aryl wherein the alkyl and aryl moieties independently are optionally substituted.

[0016] The term "heteroaralkyl" refers to an alkyl group substituted with a heteroaryl wherein the alkyl and heteroaryl moieties independently are optionally substituted.

[0017] The term "substituted" in the expression of "substituted or unsubstituted" described herein means that one or more hydrogen atoms in the hydrocarbon are each independently replaced by the same or different substituents. Suitable substituents may include, but are not limited to -F; -Cl; -Br; -CN; -NO_2; -OH; =O; C_1-C_{20} alkyl unsubstituted or substituted with -F, -Cl, -Br, -CN, -NO_2, -OH or =O; C_1-C_{20} alkoxy unsubstituted or substituted with -F, -Cl, -Br, -CN, -NO_2, -OH or =O; C_6-C_{30} aryl unsubstituted or substituted with C_1-C_{20} alkyl, C_1-C_{20} alkoxy, -F, -Cl, -Br, -CN, -NO_2, - OH or =O; C_6-C_{30} heteroaryl unsubstituted or substituted with C_1-C_{20} alkyl, C_1-C_{20} alkoxy, -F, -Cl, -Br, -CN, -NO_2, -OH or =O; C_5-C_{20} cycloalkyl unsubstituted or substituted with C_1-C_{20} alkyl, C_1-C_{20} alkoxy, -F, -Cl, -Br, -CN, -NO_2, -OH or =O; C_5-C_{30} heterocycloalkyl unsubstituted or substituted with C_1-C_{20} alkyl, C_1-C_{20} alkoxy, -F, -Cl, - Br, -CN, -NO_2, -OH or =O; C_1-C_{20} alkoxysilane unsubstituted or substituted with -F, -Cl, -Br, -CN, -NO_2, -OH or =O; and groups represented by -N(G1)(G2) (wherein G1 and G2 are each independently hydrogen, C_1-C_{10} alkyl or C_6-C_{30} aryl unsubstituted or substituted with C_3-C_{10} alkyl.

[0018] The term "derivative" of a certain substance described herein means a compound prepared by substitution of some hydrogen atoms in the certain substance with the above-described substituents.

[0019] The present invention provides an electroless silver plating solution including a silver complex solution and a reducing agent solution wherein the silver complex solution includes a silver carboxylate represented by Formula 1:

[Formula 1] R_1-COOAg

wherein R_1 is hydrogen, substituted or unsubstituted C_1-C_{22} alkyl, substituted or unsubstituted C_3-C_{30} cycloalkyl, substituted or unsubstituted C_6-C_{30} aralkyl, substituted or unsubstituted C_1-C_{30} heteroalkyl, substituted or unsubstituted C_2-C_{30} heterocycloalkyl or substituted or unsubstituted C_5-C_{30} heteroaralkyl, and the electroless silver plating is based on a silver mirror reaction between the silver complex solution and the reducing agent solution.

[0020] Specifically, the silver plating solution of the present invention includes, as major components, a silver carboxylate represented by Formula 1:

[Formula 1] R_1-COOAg

wherein R_1 is hydrogen, substituted or unsubstituted C_1-C_{22} alkyl, substituted or unsubstituted C_3-C_{30} cycloalkyl, substituted or unsubstituted C_6-C_{30} aralkyl, substituted or unsubstituted C_1-C_{30} heteroalkyl, substituted or unsubstituted C_2-C_{30} heterocycloalkyl or substituted or unsubstituted C_5-C_{30} heteroaralkyl, and a nitrogen-containing complexing agent.

[0021] The present invention also provides various conductive products and silver mirror products manufactured using the silver plating solution.

[0022] R_1 in Formula 1 may be, for example, hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, t-butyl, n-pentyl, iso-amyl, t-amyl, n-hexyl, 2-ethylhexyl, n-heptyl, octyl, iso-octyl, nonyl, decyl, neodecyl, dodecyl, tetradecyl, hexadecyl, octadecyl, docosanyl, oleyl, linoleyl, cyclopropyl, cyclopentyl or cyclohexyl.

[0023] The silver carboxylate of Formula 1 is a silver precursor, and specific examples thereof include silver acetate, silver propionate, silver trifluoroacetate, silver lactate, silver malonate, silver maleate, silver fumarate, silver pyruvate, silver succinate, silver picrate, silver citrate, silver 2-ethylhexanoate, silver neodecanoate, silver stearate, silver docosanoate, silver oleate, silver linoleate, and silver cyclohexane carboxylate. Silver acetate and silver alkanoates such as silver propionate and silver neodecanoate are most preferable from a comprehensive point of view, including economic efficiency, stability, and dissolution characteristics that are required in the present invention.

[0024] The amount of silver used is not particularly limited as long as it does not impair the object of the present

invention and is typically 0.05 to 5.0% by weight, preferably 0.1 to 3.0% by weight, more preferably 0.2 to 2.0% by weight, based on the weight of the final plating solution. If the amount of silver is less than the lower limit or exceeds the upper limit, the economic efficiency and stability of the plating solution may be poor or the quality of the final product may deteriorate.

[0025] The complexing agent binds to silver ions in the silver plating solution to form stable complex ions, which are readily dissolved at a high concentration in a solvent. The complexing agent mainly acts as an electron donor. The complexing agent is preferably a compound containing at least one nitrogen, phosphorus or sulfur atom. A nitrogen-containing compound is more preferable in terms of stability and economic efficiency.

[0026] For example, the nitrogen-containing compound may be selected from the group consisting of ammonia, amines (including primary, secondary, and tertiary amines), quaternary ammonium salts, polyamines, and mixtures thereof. A substituted or unsubstituted C_1-C_{20} alkyl, aryl or aralkyl group may be bonded to the nitrogen atom of the nitrogen-containing compound.

[0027] The alkyl group may be of any type such as a linear, branched, comb, star-shaped, dendritic or cyclic type. The nitrogen-containing compound may have a functional group such as a hydroxyl, alkoxy, ester, amide or urethane group.

[0028] In one embodiment, the nitrogen-containing compound may be ammonia, an amine compound represented by Formula 2:

[Formula 2] $(R_2R_3R_4)N$

wherein R_2 to R_4 are the same as or different from each other and are each independently hydrogen, substituted or unsubstituted C_1-C_{20} alkyl, substituted or unsubstituted C_6-C_{30} aryl, substituted or unsubstituted C_3-C_{30} cycloalkyl, substituted or unsubstituted C_6-C_{30} aralkyl, substituted or unsubstituted C_1-C_{30} heteroalkyl, substituted or unsubstituted C_2-C_{30} heterocycloalkyl, substituted or unsubstituted C_5-C_{30} heteroaryl or substituted or unsubstituted C_5-C_{30} heteroaralkyl, or a quaternary ammonium salt compound represented by Formula 3:

[Formula 3] $(R_5R_6R_7R_8)N^+X$

wherein R_5 to R_8 are as defined for R_2 to R_4 in Formula 2 and X is F^-, Cl^-, Br^-, I^-, OH^-, hydrogen sulfate, bicarbonate, carbamate or perchlorate.

[0029] Specifically, the nitrogen-containing compound may be selected from ammonia, methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, isobutylamine, tert-butylamine, n-pentylamine, iso-pentylamine, tert-amylamine, n-hexylamine, diethylamine, triethylamine, 2-ethylhexylamine, cyclohexylamine, allylamine, propargylamine, ethylenediamine, 1,3-propylenediamine, hexamethylenediamine, triethylenediamine, 1,2-diaminopropane, monoethanolamine, diethanolamine, 1-amino-2-propanol, 3-amino-1-propanol, 1,4-butanediamine, spermine, spermidine, diethylenetriamine, triethylenetetramine, tris(2-aminoethyl)amine, 1,1,1-tris(aminomethyl)ethane, N,N-diethylhydroxyamine, methoxyethylamine, N,N-diethylethylenediamine, N,N,N',N'-tetramethylethylenediamine, pyridine, piperidine, piperazine, morpholine, imidazole, pyrrole, quinuclidine, benzylamine, phenethylamine, ammonium carbamate, ammonium carbonate, tetraethylammonium bicarbonate, tetraethyl ammonium bromide, tetrabutylammonium hydroxide, aminopropyltriethoxysilane, polyethyleneimine (PEI), poly(propyleneimine), polyvinylamine (PVAm), poly(amidoamine) (PAMAM), and derivatives thereof. In one embodiment, the plating solution may be an aqueous alkaline solution containing an ethylenediaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA) compound, for example, disodium EDTA, trisodium EDTA, tetrasodium EDTA, sodium NTA or trisodium NTA, succinimide, maleimide, phthalimide, ethylenediamine, hexamethylenetetramine, saccharin, imidazole, oxazoline, hydantoin, 5,5-dimethylhydantoin or a mixture thereof. The nitrogen-containing compound is most preferably ammonia or an alkylamine such as methylamine or ethylamine in terms of economic efficiency and characteristics that are required in the present invention.

[0030] The amount of the complexing agent used is not particularly limited as long as it does not impair the object of the present invention. The complexing agent is typically used in a molar ratio 0.1-10.0, preferably 0.3-7.0, more preferably 0.5-5.0 relative to the silver carboxylate. If the amount of the complexing agent is less than the lower limit or exceeds the upper limit, the stability of the plating solution may be problematic or the reaction may not be completed, resulting in deterioration of quality.

[0031] The silver plating solution of the present invention may use water, ethanol, ethylene glycol, glycerin or a mixture thereof as a solvent. That is, the silver plating solution may be an alcohol or glycol-containing aqueous solution and may have very high wettability. Accordingly, the silver plating solution can be used to easily plate metals and metal alloys such as copper, nickel, zinc, tin, antimony, molybdenum, platinum, bronze, and brass, oxides and sulfides of these metals, ceramics such as silica, alumina, titanium oxide, mica, clay, and glass, plastics such as polyesters, nylons, polyimides, polyurethanes, and acrylics, various carbon compounds such as carbon, carbon nanotubes, graphite, and graphene, various types of substrates such as rubbers, nonwoven fabrics, and paper, and particles, flakes, beads,

sheets, foils, films, and fibers thereof regardless of their forms or shapes.

[0032] Silver mirror reaction tests with Tollens' reagent are inconvenient in that a new silver solution should be prepared and used for each silver mirror reaction. In contrast, the silver plating solution of the present invention can be prepared and stored in advance for use whenever needed. The silver plating solution of the present invention is not necessarily limited to a specific hydrogen ion concentration (pH). General silver plating processes (including electroless silver plating) are performed in a relatively strongly acidic (pH $\leq$ 3.0) or alkaline range (pH $\geq$ 10.0). In contrast, the present invention features that silver plating is performed well even in a neutral to weakly alkaline range (pH 7.0-9.0), except for special cases. That is, due to its environmental friendliness and good storage stability, the silver plating solution of the present invention can be stored before use and can be conveniently used for experiments whenever desired. Another feature of the silver plating solution according to the present invention is that when it is intended to conduct an exemplary redox reaction experiment at school or manufacture a silver mirror souvenir or ornament, the silver plating solution is very useful for anyone because of its simplicity and safety. In addition, the silver plating solution of the present invention can be used to manufacture a silver mirror with low surface roughness because it does not use tin chloride. Above all, the silver plating solution of the present invention is very suitable for use in the manufacture of high-quality optical mirrors such as telephoto lenses.

[0033] The features of the present invention can be better achieved when the silver plating solution including the silver carboxylate as a silver precursor and the complexing agent further includes a stabilizer, a solvent, and additives. Particularly, a reducing agent is essential for electroless silver plating or silver mirror reaction.

[0034] The reducing agent serves to transfer electrons released during its oxidation to silver ions such that silver is deposited on the surface of an object. Specific examples of suitable reducing agent for use in the silver plating solution of the present invention include acetol, acetoin, hydroxyacetone, hydroxylamine, diethylhydroxylamine, methylethylketoxime, Rochelle salt, sodium erythorbate, ammonia borane, alkylaminoboranes such as methylaminoborane and diethylaminoborane, hydrazine, hydrazine hydrate, hydrazine sulfate, sodium hypophosphite, sodium sulfite, sodium thiosulfate, sodium borohydride, lithium aluminum hydride, sodium citrate, and alkylamines such as butylamine, ethanolamine, ethylenediamine, and dodecylamine, ethylene glycol, thiodiglycol, diethylene glycol, formaldehyde, glucose, sorbitol, sugars, formic acid, ammonium formate, triethylammonium formate, tetramethylammonium formate, citric acid, ascorbic acid, tartaric acid, phenidone, 2-((4-amino-3-methylphenyl)ethylamino)ethyl sulfate, N-(2-((4-amino-3-methylphenyl)ethylamino)ethyl)methanesulfonamide, 4-(N-ethyl-N-2-hydroxyethyl)-2-methylphenylenediamine sulfate, hydroquinone compounds such as methylhydroquinone, methoxyhydroquinone, t-butylhydroquinone, 2,5-di-t-butylhydroquinone, 2,5-bis(1,1-dimethylbutyl)hydroquinone, and 2,5-bis(1,1,3,3-tetramethylbutyl)hydroquinone, and phenolic and polyphenolic compounds such as 4-methoxyphenol, 2,6-di-t-butyl-4-methylphenol, quinhydrone, p-methylaminophenol sulfate, p-aminophenol, diaminophenol, 2-naphthol, catechol, t-butylcatechol, resorcinol, phloroglucinol, hydroxyquinol, pyrogallol, tannin, tannic acid, dopamine, cardanol, urushiol, gallic acid and its derivatives, flavonoid, isoflavone, and anthocyanin. These reducing agents may be used alone or as a mixture of two or more thereof. Representative examples of these reducing agents include glucose, hydrazine, hydroquinone, and derivatives thereof. Hydroquinone is most preferable in terms of various aspects, including reaction rate, environmental friendliness, and safety that are required in the present invention, because glucose reacts slowly and hydrazine reacts fast but is harmful to humans. Apart from these reducing agents, heat, light, plasma, infrared (IR), ultraviolet (UV), electron beam, photon, laser, microwave, electrical, and magnetic treatments also act like reducing agents. Accordingly, these treatments are performed alone or in combination with the reducing agent for faster reduction. The amount of the reducing agent used is not particularly limited as long as it does not impair the object of the present invention and is typically in a molar ratio of 0.1-5.0, preferably 0.3-3.0, more preferably 0.5-2.0 relative to the silver carboxylate. If the amount of the reducing agent is less than the lower limit or exceeds the upper limit, the stability of the plating solution may be problematic or the reaction may proceed too slowly or too fast, making it difficult to control the reaction and deteriorating product quality.

[0035] The reaction temperature during silver plating is not particularly limited as long as it does not impair the object of the present invention and is typically 5 to 50 °C, preferably 10 to 40 °C, more preferably 15 to 30 °C. If the reaction temperature is lower than the lower limit or higher than the upper limit, the stability of the plating solution may deteriorate or the reaction may proceed too slowly or too fast, making it difficult to control the reaction and deteriorating product quality.

[0036] The stabilizer may be selected from long-chain mercaptans such as dodecanethiol, fatty acids such as oleic acid, amines such as oleylamine, polymers such as polyvinylpyrrolidone, poly(2-ethyl-2-oxazoline), polyvinyl alcohol, polyethylene glycol, and polystyrene sulfonic acid and their copolymers, and synthetic and natural polymers such as carboxymethyl cellulose, alginic acid, chitosan, dopamine, starch, polysaccharide, and gums. The use of the stabilizer can be expected to prevent changes over time or effectively improve adhesiveness. The additives may be a surfactant and an anti-tarnish agent. The surfactant is preferably a nonionic surfactant such as a polyoxyethylene alkyl ether or ester, a fatty acid sorbitan ester or an alkyl monoglyceryl ether. The anti-tarnish agent may be selected from the group consisting of benzotriazole and derivatives thereof. One or more other additives selected from the group consisting of metal compounds such as ammonium molybdate, bismuth nitrate, selenic acid, and thallium nitrate and mixtures thereof may also be used in the present invention.

[0037] For electroless silver plating based on a silver mirror reaction, the silver plating solution of the present invention may use an ammonium salt as an additive. In this case, the ammonium salt may be ammonium formate, ammonium acetate, ammonium nitrate, ammonium sulfate, ammonium sulfite, ammonium carbonate, ammonium bicarbonate, ammonium carbamate or ammonium phosphate. An appropriate use of the ammonium salt enables control over reaction rate to ensure uniform plating, improved mirror characteristics, and high conductivity. The amount of the ammonium salt used is not particularly limited as long as it does not impair the object of the present invention and is typically 0.01 to 10.0% by weight, preferably 0.05 to 5.0%, more preferably 0.1 to 3.0%, based on the weight of the final plating solution. If the amount of the ammonium salt is less than the lower limit or exceeds the upper limit, the stability of the plating solution may be poor or the quality of the final product may deteriorate.

[0038] The solvent is not necessarily limited as long as it does not impair the object of the present invention and may be selected from the group consisting of polar solvents, for example, deionized water, alcohols such as methanol, ethanol, n-propanol, iso-propanol, n-butanol, iso-butanol, 1-methoxy-2-propanol, diacetone alcohol, 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol, glycols and glycol ethers such as ethylene glycol, diethylene glycol, propylene glycol, glycerin, ethylene glycol monobutyl ether, propylene glycol monomethyl ether, and diethylene glycol monoethyl ether, ionic liquids such as ethylammonium nitrate and 1-ethyl-3-methylimidazolium dicyanamide, and mixtures thereof. Water, ethanol, ethylene glycol, glycerin or a mixture thereof, particularly, a mixed solvent of water and ethanol is most suitable for use in the present invention. The use of a minimum amount of water for silver electroplating ensures high plating quality. As the content of water increases upon electroless plating based on a silver mirror reaction, the reaction rate increases and the lifetime of the plating solution decreases. If the content of water is excessively high, the stability of the plating solution may deteriorate and the quality of the final product may not be uniform. Thus, the content of water is preferably limited to 1 to 80% by weight, more preferably 20 to 50% by weight, based on the total weight of the solvents.

[0039] A nonconductor such as glass, ceramic or plastic may be cleaned with nitric acid, a surfactant or an alcohol before electroless silver plating. After cleaning, a suitable process selected from mechanical polishing such as vapor blasting or grinding with silicon carbide, etching with chromic acid, sulfuric acid or hydrofluoric acid, and sensitization and activation with tin chloride ($SnCl_2$) and palladium chloride ($PdCl_2$) may be used to improve adhesion. In contrast, since an alcoholic solution is mainly used and autocatalytic plating of silver ions occurs in the silver plating solution of the present invention, electroless plating based on a silver mirror reaction proceeds well while maintaining the adhesion to some extent even without the need for the pretreatment processes described above. Subsequently, electroplating may be performed on the electroless-plated material as a cathode to increase the plating thickness or achieve better appearance and physical properties.

[0040] A copper substrate is prone to displacement plating even without a reducing agent solution. Thus, the silver complex solution can be used alone for electroless plating. For electroplating, the silver complex solution may be used as an electrolyte. In this case, electricity is used for silver plating instead of a reducing agent.

[0041] After silver plating is completed, silver and silver alloys are generally protected from discoloration by the use of a commercially available anti-tarnish product such as Tarniban, surface coating with a sulfur compound such as a thiol or sulfide, immersion in an anhydrous chromic acid solution or cathodic treatment in an alkaline chromic acid solution. Thermal treatment may be further performed at 50 to 150 °C for quality stabilization and impurity removal depending on the type of the final product. The thermally treated product may be dipped in a polymeric compound such as a water-based polyurethane, water-based acrylic polymer, polyester, silicone polymer or fluorinated polymer, coated by a wet process such as spray coating, spin coating, bar coating, slit-die coating or gravure coating, or subjected to vacuum deposition or sputtering with an inorganic compound such as silica or titanium dioxide depending on the type of the final product.

[0042] The present invention will be explained in more detail with reference to the following examples. However, these examples are provided for illustrative purposes and do not serve to limit the scope of the invention.

[EXAMPLES]

[0043] In the following examples, including preparative examples 1-13, unless otherwise mentioned, all experiments were conducted at room temperature of 25 °C. All percentages are by weight, unless otherwise specified.

Preparation of Silver Complex Solutions for Silver Plating

Preparative Example 1

[0044] 40 g of aqueous ammonia (28-30%) was slowly added to 100 g of silver neodecanoate, followed by complete dissolution. To the solution was added 70 g of ethanol (95%). Filtration gave a silver neodecanoate-ammonia complex solution (final silver content: ~ 18.0%).

Preparative Example 2

[0045] A mixed solution of 280 g of ethanol and 70 g of deionized water (hereinafter referred to simply as "water") was added to 10 g of the silver neodecanoate-ammonia complex solution prepared in Preparative Example 1 to prepare a colorless and transparent silver neodecanoate-ammonia complex solution (final silver content: 0.5%).

Preparative Example 3

[0046] 350 g of ethanol was added to 10 g of the silver neodecanoate-ammonia complex solution prepared in Preparative Example 1 to prepare a silver neodecanoate-ammonia complex solution (final silver content: 0.5%).

Preparative Example 4

[0047] 2.0 g of aqueous ammonia was added to 100 g of the silver neodecanoate-ammonia complex solution prepared in Preparative Example 2 to prepare a silver complex solution.

Preparation of Reducing Agent Solutions

Preparative Example 5

[0048] 1.5 g of hydroquinone was added to a mixed solution of 100 g of ethanol and 400 g of water to prepare a reducing agent solution.

Preparative Example 6

[0049] 1.5 g of hydroquinone was added to a mixed solution of 100 g of glycerin and 400 g of water to prepare a reducing agent solution.

Preparative Example 7

[0050] 1.5 g of hydroquinone was added to a mixed solution of 400 g of ethanol and 100 g of water to prepare a reducing agent solution.

Preparative Example 8

[0051] 3.0 g of 2,5-di-tert-butylhydroquinone was added to a mixed solution of 250 g of ethanol and 250 g of water to prepare a reducing agent solution.

Preparative Example 9

[0052] 0.5 g of ammonium formate was added to 100 g of the reducing agent solution prepared in Preparative Example 5 to prepare a reducing agent solution.

Preparative Example 10

[0053] 0.5 g of 80% hydrazine hydrate was added to 100 g of water to prepare a reducing agent solution.

Preparative Example 11

[0054] 5.0 g of glucose was added to 100 g of water to prepare a reducing agent solution.

Preparative Example 12

[0055] 0.5 g of 80% hydrazine hydrate was added to a mixed solution of 50 g of water and 50 g of ethanol, and 0.5 g of ammonium nitrate was added thereto to prepare a reducing agent solution.

Preparative Example 13

[0056] 0.5 g of 80% hydrazine hydrate was added to 100 g of water, and 0.5 g of ammonium formate was added thereto to prepare a reducing agent solution.

Manufacture of Silver Mirror Products

Example 1

[0057] First, about half the volume of a pre-cleaned transparent glass container with a lid was filled with the silver complex solution of Preparative Example 2. The container was sufficiently shaken to sensitize and activate its inner surface. Thereafter, the other half of the container was filled with the reducing agent solution of Preparative Example 5. The container was sufficiently shaken and left standing for ~30 min. The content of the container was discharged, followed by sufficient washing with ethanol. As a result, a light gold-colored mirror was formed on the inner surface of the container and a clean silver mirror was formed on the outer surface of the container. The inner surface of the container was coated with a water-based polyurethane for discoloration prevention. A photograph of the resulting sample is shown in Fig. 1.

Example 2

[0058] The procedure of Example 1 was repeated except that the reducing agent solution of Preparative Example 6 was used instead of the reducing agent solution of Preparative Example 5. As a result, the reaction was slightly slower than that in Example 1, and a light black mirror was well formed on the inner surface of the container and a clean silver mirror was well formed on the outer surface of the container. The inner surface of the container was coated with a water-based acrylic polymer for discoloration prevention. A photograph of the resulting sample is shown in Fig. 1.

Example 3

[0059] The procedure of Example 1 was repeated except that the reducing agent solution of Preparative Example 7 was used instead of the reducing agent solution of Preparative Example 5. As a result, the reaction was slightly slower than that in Example 1, and a clean silver mirror was well formed on each of the inner and outer surfaces of the container. A photograph of the resulting sample is shown in Fig. 1.

Example 4

[0060] The procedure of Example 1 was repeated except that the reducing agent solution of Preparative Example 8 was used instead of the reducing agent solution of Preparative Example 5. As a result, a clean silver mirror was well formed on each of the inner and outer surfaces of the container. A photograph of the resulting sample is shown in Fig. 1.

Example 5

[0061] First, about half the volume of a pre-cleaned transparent glass container with a lid was filled with the silver complex solution of Preparative Example 3. The container was sufficiently shaken to sensitize and activate its inner surface. Thereafter, the other half of the container was filled with the reducing agent solution of Preparative Example 6. The container was sufficiently shaken and left standing for ~1 h. The content of the container was discharged, followed by sufficient washing with ethanol. As a result, a gold-colored mirror was well formed on the inner surface of the container and a clean silver mirror was well formed on the outer surface of the container. The inner surface of the container was coated with a silicone-based polymer for discoloration prevention. A photograph of the resulting sample is shown in Fig. 1.

Example 6

[0062] First, about half the volume of a pre-cleaned transparent glass container with a lid was filled with the silver complex solution of Preparative Example 2. The container was sufficiently shaken to sensitize and activate its inner surface. Thereafter, the other half of the container was filled with the reducing agent solution of Preparative Example 9. The container was sufficiently shaken and left standing for ~1 h. The content of the container was discharged, followed by sufficient washing with ethanol. As a result, a black mirror was well formed on the inner surface of the container and a clean silver mirror was well formed on the outer surface of the container. A photograph of the resulting sample is shown in Fig. 1.

Example 7

[0063] The procedure of Example 6 was repeated except that the silver complex solution of Preparative Example 4 was used instead of the silver complex solution of Preparative Example 2. As a result, a light gold-colored silver mirror was well formed on the inner surface of the container and a clean silver mirror was well formed on the outer surface of the container. A photograph of the resulting sample is shown in Fig. 1.

Example 8

[0064] The procedure of Example 1 was repeated except that a transparent polyester container (PET bottle) was used instead of the pre-cleaned transparent glass container with a lid. As a result, a light gold-colored mirror was formed on the inner surface of the container and a clean silver mirror was formed on the outer surface of the container. A photograph of the resulting sample is shown in Fig. 3.

Example 9

[0065] First, about half the volume of a pre-cleaned transparent glass container with a lid was filled with the silver complex solution of Preparative Example 3. The container was sufficiently shaken to sensitize and activate its inner surface. Thereafter, the other half of the container was filled with the reducing agent solution of Preparative Example 10. The container was sufficiently shaken and left standing for ~10 min. The content of the container was discharged, followed by sufficient washing with water. As a result, a bright light gold-colored mirror and a silver mirror were formed on the inner and outer surfaces of the container, respectively. The mirrors were thinner than those formed when the hydroquinone reducing agent was used.

Example 10

[0066] First, about half the volume of a pre-cleaned transparent glass container with a lid was filled with the silver complex solution of Preparative Example 3. The container was sufficiently shaken to sensitize and activate its inner surface. Thereafter, the other half of the container was filled with the reducing agent solution of Preparative Example 11. The container was sufficiently shaken and left standing for ~6 h. The content of the container was discharged, followed by sufficient sequential washing with water and ethanol. As a result, a bright gold-colored mirror and a silver mirror were formed on the inner and outer surfaces of the container, respectively. The mirrors were thinner than those formed when the hydroquinone reducing agent was used.

Example 11

[0067] In Preparative Example 1, 60 g of an aqueous methylamine solution (40%) was used instead of the aqueous ammonia as a complexing agent. The silver neodecanoate was completely dissolved and 80 g of ethanol was added thereto. Filtration gave a purple silver neodecanoate-methylamine complex solution. 300 g of ethanol was added to 10 g of the complex solution to prepare a colorless complex solution (final silver content: ~0.5%). The complex solution was placed in a pre-cleaned transparent glass container with a lid. The container was sufficiently shaken to sensitize and activate its inner surface. Thereafter, the container was filled with the same amount of the reducing agent solution of Preparative Example 13 based on the weight ratio. The container was sufficiently shaken and left standing for ~10 min. The content of the container was discharged, followed by sufficient sequential washing with water and ethanol. As a result, a black and dark gold-colored mirror was well formed on the inner surface of the container and a bright silver mirror was well formed on the outer surface of the container.

Example 12

[0068] The procedure of Example 11 was repeated except that the reducing agent solution of Preparative Example 11 was used instead of the reducing agent solution of Preparative Example 13. After 1 h, a bright silver mirror was formed well on the inner surface of the container and a bright silver mirror was well formed on the outer surface of the container.

Comparative Example 1

[0069] A colorless alcoholic ammonia complex solution (final silver content: 0.5%) was prepared in the same manner as in Preparative Example 1, except that silver neodecanoate was dissolved in alcoholic ammonia instead of the aqueous

ammonia and absolute ethanol was used as a diluent. The colorless alcoholic ammonia complex solution was sufficiently shaken in a pre-cleaned transparent glass container with a lid to sensitize and activate the inner surface of the container. Thereafter, the container was filled with the same amount of a reducing agent solution, which had been previously prepared by dissolving 0.3% hydroquinone in absolute ethanol, based on the weight ratio. The reaction was allowed to proceed for 30 min. As a result, a dark silver mirror was formed with lower quality than the silver mirror formed when 95% ethanol was used.

Comparative Example 2

[0070] An aqueous silver neodecanoate-ammonia complex solution (final silver content: 0.5%) was prepared in the same manner as in Preparative Example 1, except that water was continuously added instead of ethanol. However, a white solid was precipitated, making it impossible for the silver mirror reaction to proceed further.

Examples 13-19

[0071] Experiments were conducted to determine whether plating was successfully performed depending on the silver content. Silver mirror products were manufactured in the same manner as in Example 1, except that the amount of ethanol mixed with the complex solution was adjusted such that the final silver content was as shown in Table 1. The content of water was fixed to 70 g as in Preparative Example 2.

[Table 1]

	Complex solution (g)	Ethanol (g)	Final silver content (%)
Example 13	2	3528	0.01
Example 14	10	3520	0.05
Example 15	20	3510	0.1
Example 16	10	280	0.5
Example 17	20	270	1
Example 18	10	28	5
Example 19	75	35	7.5

[0072] The complex solution was placed in a pre-cleaned transparent glass container with a lid. The container was sufficiently shaken to sensitize and activate its inner surface. Thereafter, the container was filled with the same amount of the reducing agent solution of Preparative Example 5 based on the weight ratio. The container was sufficiently shaken and left standing for ~10 min. The content of the container was discharged, followed by sufficient sequential washing with water and ethanol. A determination was made as to whether the silver mirror reaction proceeded depending on the final silver content.

[0073] The experiments revealed that the silver mirror reaction was most stable to achieve clean plating in Example 16 and the silver mirrors were formed despite their low silver contents in Examples 14 and 15. In Example 13, the silver mirror reaction was performed even when the silver content was as low as 0.01%, but the silver mirror was semi-transparent with poor mirror characteristics.

[0074] In contrast, the colors of the silver mirrors with high silver contents formed in Examples 17 and 18 became darker with increasing silver content. The silver mirror with a silver content of 7.5% formed in Example 19 was dark in color and silver was precipitated on the bottom of the container.

Example 20

[0075] In Preparative Example 1, 15 g of aqueous ammonia was slowly added to 20 g of silver acetate instead of silver neodecanoate. The silver acetate was completely dissolved and 15 g of ethanol was added thereto. Filtration gave a colorless silver acetate-ammonia complex solution. 500 g of ethanol was added to 10 g of the complex solution to prepare a colorless complex solution (final silver content: ~0.5%). The silver acetate solution was placed in a pre-cleaned transparent glass container with a lid. The container was sufficiently shaken to sensitize and activate its inner surface. Thereafter, the container was filled with the same amount of the reducing agent solution of Preparative Example 13 based on the weight ratio. The container was continuously shaken. As a result, a bright silver mirror was well formed within 5 min. The content of the container was discharged, followed by sufficient sequential washing with water and

ethanol. As a result, a gold-colored mirror was well formed on the inner surface of the container and a bright silver mirror was well formed on the outer surface of the container.

Examples 21-26

[0076] Experiments were conducted in the same manner as in Example 20 to determine whether silver mirror reactions occurred depending on the silver carboxylates shown in Table 2.

[Table 2]

	Silver carboxylate	Occurrence of silver mirror reaction
Example 21	Silver propionate	○
Example 22	Silver 2-ethylhexanoate	○
Example 23	Silver malonate	Δ
Example 24	Silver lactate	Δ
Example 25	Silver oleate	Δ
Example 26	Silver nitrate	Δ

[0077] As can be seen from the results in Table 2, when silver propionate or silver 2-ethylhexanoate was used, silver mirror reactions proceeded relatively smoothly under appropriate reaction conditions, like when silver neodecanoate and silver acetate were used in Examples 1-20. Silver mirror reactions were performed even when different kinds of silver carboxylates were used. However, weak silver mirror reactions occurred under general conditions due to their low reactivity. That is, the different kinds of silver carboxylates also allowed silver mirror reactions to proceed at a level comparable to or better than that achieved by silver nitrate, which has been widely used for this purpose.

Examples 27-33

[0078] Experiments were conducted in the same manner as in Example 20 to determine whether plating was successfully performed depending on the content of the complexing agent. Silver mirror products were manufactured in the same manner as in Preparative Example 1 and Example 1, except that the amount of the complexing agent (aqueous ammonia) mixed with the silver carboxylate (silver neodecanoate) in the complex solution was adjusted as shown in Table 3.

[Table 3]

	Silver carboxylate (g)	Aqueous ammonia (g)	Weight ratio
Example 27	100	1	0.01
Example 28	100	4	0.04
Example 29	100	20	0.20
Example 30	100	40	0.40
Example 31	100	80	0.80
Example 32	100	120	1.20
Example 33	100	200	2.00

[0079] Silver mirror reactions were carried out in the same manner as in Example 1, except that the silver carboxylate and the complexing agent were mixed in the same ratios shown in Table 3. In Examples 27 and 28 where the content of the complexing agent was low, there was a solubility problem and the silver mirror reaction hardly occurred. In Examples 29-32, the silver mirror reactions normally occurred. The best silver mirror was formed in Example 30.

[0080] In Example 33 where the complexing agent was used in excess, the complex solution of the complexing agent and the silver carboxylate had poor storage stability and a clean silver mirror was difficult to obtain.

Examples 34-40

[0081] Experiments were conducted in the same manner as in Example 1 to determine whether plating was successfully performed depending on the content of the reducing agent, except that the silver complex and the reducing agent were mixed in the amounts shown in Table 4 and the same amount (10 g) of the mixture was fed into a container.

[Table 4]

	Silver complex (g)	Reducing agent (g)	Weight ratio
Example 34	100	5	0.05
Example 35	100	10	0.10
Example 36	50	20	0.40
Example 37	50	50	1.00
Example 38	40	80	2.00
Example 39	20	100	5.00
Example 40	20	120	6.00

[0082] Each of the mixtures of the silver complex solution and the reducing agent solution in the ratios shown in Table 4 was fed into a container. In Examples 35-39, desired silver mirror reactions normally occurred. The rate of the silver mirror reaction increased with increasing content of the reducing agent. In Example 34 where the content of the reducing agent was low, the silver mirror reaction time was long (~50-80 min), making it difficult to use the silver mirror for industrial applications. In Example 40 where the reducing agent was used in excess, silver was precipitated and the silver mirror was semi-transparent with poor mirror characteristics due to the relatively low silver content.

Manufacture of Conductive Products

Example 41

[0083] The silver neodecanoate-ammonia complex solution (silver content: 18.0%) prepared in Preparative Example 1 was diluted to a final silver content of 1.0% with a mixed solution of ethanol and water in a 4:1 weight ratio. 0.5% ammonium formate was dissolved in the dilute silver neodecanoate-ammonia complex solution to prepare an electroless silver plating solution. 3.0 g of hydroquinone was added to a mixed solution of 100 g of glycerin and 400 g of water to prepare a reducing agent solution. A nylon fabric was sufficiently wetted with the silver plating solution by immersion for 1 h, and then the reducing agent solution was added thereto in a weight ratio of 1:1 to the silver plating solution. The reaction was allowed to proceed with stirring for 3 h. After completion of the reaction, the nylon fabric was filtered, washed sequentially with water and ethanol, and dried at 120 °C for 12 h to manufacture a silver-coated nylon fabric with high conductivity (see Fig. 4).

Example 42

[0084] A silver-coated nylon fiber with high conductivity was manufactured in the same manner as in Example 41, except that a nylon fiber was used instead of the nylon fabric. Fig. 5 shows a photograph of the resulting sample and the measured conductivity of the sample. Fig. 6 show a surface scanning electron microscopy (SEM) image of the fiber.

Example 43

[0085] A silver-coated mirror-like polyimide film was manufactured in the same manner as in Example 41, except that a 25 micron polyimide film was used instead of the nylon fabric. Fig. 7 shows a photograph of the resulting sample. The reflectance and sheet resistance of the sample were measured to be 97.5% at 550 nm and 120 mΩ/□, respectively.

Example 44

[0086] A silver-coated mirror-like nylon film was manufactured in the same manner as in Example 43, except that a 12 micron nylon film was used instead of the 25 micron polyimide film. The sheet resistance of the film was measured to be 130 mΩ/□.

Example 45

[0087] The silver neodecanoate-ammonia complex solution (silver content: 18.0%) prepared in Preparative Example 1 was diluted with a mixed solution of ethanol and water in a 1:1 weight ratio to prepare an electroless silver plating solution (final silver content: 0.5%). A polyurethane foam was sufficiently wetted with the silver plating solution for 1 h, and then the reducing agent solution of Preparative Example 12 was added thereto in a weight ratio of 1:1 to the silver plating solution. The reaction was allowed to proceed with stirring for 2 h. After completion of the reaction, the polyurethane foam was filtered, washed sequentially with water and ethanol, and dried at 120 °C for 30 min to manufacture a silver-coated polyurethane foam whose surface resistance was measured to be 0.3 Ω/cm. A photograph and a surface scanning electron microscopy (SEM) image of the silver-coated sample are shown in Figs. 8 and 9, respectively.

Example 46

[0088] Silica beads having an average particle diameter of 12 μm and surface treated with 3-aminotriethoxysilane were added to and sufficiently wetted with the silver complex solution of Preparative Example 3 with stirring, filtered, washed with ethanol, and dried. The pretreated silica beads were added to an electroless silver plating solution composed of the silver complex solution of Preparative Example 4 and the reducing agent solution of Preparative Example 9 in a 1:1 weight ratio. The reaction was allowed to proceed with stirring for 1 h. After completion of the reaction, the silica beads was filtered, washed sequentially with water and ethanol, and dried at 100 °C for 24 h to manufacture silver-coated silica beads.

Example 47

[0089] Silver-coated copper particles were manufactured in the same manner as in Example 46, except that copper particles having an average particle diameter of 4 μm were used instead of the silica beads having an average particle diameter of 12 μm.

Example 48

[0090] The silver complex solution (silver concentration: 0.5%) of Preparative Example 3 was placed in a polypropylene plating bath. A silver plate and a copper foil whose surface was smooth were used as an anode and a cathode, respectively. A 4.5 V power supply was connected between the anode and cathode. The power supply consisted of three 1.5 V dry cells connected in series. Electroplating was performed for 1 min and 30 sec. After completion of the plating, the plated product was well washed with water and ethanol and sufficiently dried at 80 °C to manufacture a bright mirror-like copper product in which silver was plated on the copper surface.

Example 49

[0091] The procedure of Example 48 was repeated except that a silver-coated PET film having a resistance of 1,5 Ω/cm was used as a cathode instead of the copper foil. After electroplating, the sample was measured to have a surface resistance of 0.4 Ω/cm, indicating its improved conductivity.

Example 50

[0092] 100 g of the complex solution (silver concentration: 0.5%) prepared in Preparative Example 4 was put in a beaker and a copper foil was placed therein. In this example, none of the reducing agent solutions was used. Displacement plating was performed at room temperature for 15 min to manufacture a bright silver-coated mirror-like copper foil (see Fig. 10).

Manufacture of Antibacterial Products

Example 51

[0093] 100 g of the complex solution (silver concentration: 0.5%) of Preparative Example 2 was diluted with 4.9 kg of a mixed solution of 80% ethanol and 20% water to prepare a silver-containing mixed solution having a final concentration of 100 ppm. 100 ppm of ammonium sulfate and a white cotton fabric were added to the silver solution and the fabric was sufficiently wetted with the silver solution with stirring for 3 h. The wet fabric was squeezed to sufficiently remove the solvent and exposed to sunlight for a long time to reduce the silver ions. The color of the fabric turned to brown

depending on the degree of reduction. The fabric was washed and dried using a washing machine and its antibacterial properties were tested. As a result, the fabric showed an antibacterial activity of 99.9% against *E. coli* (see Fig. 11).

Example 52

[0094] The silver complex solution (silver concentration: 0.5%) of Preparative Example 3 was diluted with ethanol to prepare a solution (final silver concentration: 50 ppm). Polyester microfiber inserts, which are widely used as heat-insulating materials for blankets and pillows, were added to the silver solution to the extent that they were submerged in the silver solution. The polyester microfiber inserts were sufficiently wetted with the silver solution with stirring for 1 h. Then, the reducing agent solution of Preparative Example 6 was diluted with ethanol to prepare a hydroquinone solution having a final concentration of 60 ppm. The wet polyester microfiber inserts were added to the hydroquinone solution. The reaction was allowed to proceed with stirring for 1 h. After completion of the reaction, the polyester microfiber inserts were filtered, washed sequentially with water and ethanol, and dried at 80 °C for 6 h to manufacture silver-treated polyester microfiber inserts. The antibacterial properties of the microfiber inserts were tested. The microfiber inserts showed an antibacterial activity of 99.9% against *E. coli.*

Experimental Example 1

[0095] Comparisons with existing one-component electroless silver plating chemicals were undertaken. Commercial electroless silver plating chemicals AG-10 from HANBIT Chemical and MS-AG100 from MSC were used as Comparative Examples 3 and 4, respectively.

[0096] The surface of the copper-plated substrate of Example 50 was plated with silver using each of the silver plating solutions of Comparative Examples 3-4. The copper-plated substrate of Example 50 was placed in a container and the same silver complex solution as that used in Example 50 was supplied to the container. After completion of the plating, the plated surface was etched to remove silver plating formed on areas other than the copper-plated areas.

[0097] After each of the silver plating solutions of Comparative Examples 3-4 was fed into a container, the copper-plated substrate was immersed in the silver plating solution, followed by silver plating.

[0098] As a result, the same silver plating as in Example 1 could be performed when the commercial silver plating solutions of Comparative Examples 3-4 were used. The silver plating in Example 1 could be performed simply by etching to remove excess silver. This is based on the fact that a large amount of silver is deposited on the copper surface when the silver plating in Example 1 is performed, like when conventional plating processes are performed and is because silver is formed thicker on copper than on an insulator although the silver layers are etched to the same thickness. The same silver plating was performed also when the commercial silver plating solutions of Comparative Examples 3-4 were used. That is, the inventive silver plating solution can be used in conventional product manufacturing processes with slight modifications.

Experimental Example 2

[0099] The procedure of Experimental Example 1 based on the silver plating solution used in Example 1 and the commercial silver plating solutions of Comparative Examples 3-4 was repeated. A determination was made as to whether the surfaces of polymeric resins were plated.

[0100] Rectangular bars having dimensions of 1 cm × 1 cm × 3 cm were installed in a plating vessel. The rectangular bars were made of the materials shown in Table 4.

[0101] Each of the plating solution used in Example 1 and the commercial plating solutions of Comparative Examples 3-4 was added to a plating container. The container was stirred by shaking. After 20 min, the rectangular bars were taken out to determine whether they were plated.

[Table 5]

	Materials for rectangular bars	Determination of plating
Example 1	Polycarbonate	○
	Polyethylene	○
	Polypropylene	○
	Copper	○
	Aluminum	○

(continued)

	Materials for rectangular bars	Determination of plating
Comparative Example 3	Polycarbonate	×
	Polyethylene	×
	Polypropylene	×
	Copper	○
	Aluminum	○
Comparative Example 4	Polycarbonate	×
	Polyethylene	×
	Polypropylene	×
	Copper	○
	Aluminum	○

[0102] As can be seen from the results in Table 5, not only the surfaces of the rectangular bars made of metals but also the surfaces of the rectangular bars made of polymeric resins were uniformly plated with the plating solution used in Example 1. In contrast, when the plating solutions of Comparative Examples 3-4 were used, silver was plated only on the surfaces of the rectangular bars made of metals and silver plating did not occur on the surfaces of the rectangular bars made of polymeric resins.

Experimental Example 3

[0103] The silver complex solution prepared in Preparative Example 2 and the reducing agent prepared in Preparative Example 8 were stored at room temperature for 6 months and their storage stabilities were tested. Figs. 11 and 12 show the states of the silver complex solution and the reducing agent solution after storage at room temperature for 6 months, respectively.

[0104] As shown in Figs. 12 and 13, the solutions were stable without any precipitation even after storage at room temperature for 6 months. The solutions are expected to be stable even after several years.

[0105] In contrast, precipitation was observed in the plating solutions of Comparative Examples 3-4 during storage for the same time period, demonstrating that the stability of the inventive two-component silver plating solution is comparable to or higher than that of the existing one-component electroless plating solutions.

Experimental Example 4

[0106] An experiment was conducted to determine the production of silver nitrate. The contents of silver nitrate formed in the plating solutions used in Examples 1-5 and the commercial silver plating solutions of Comparative Examples 3-4 were measured.

[0107] There is no general method for determining the content of silver nitrate. Thus, a method for measuring chlorine ions using silver nitrate was reversely applied to measure content of the silver nitrate.

[0108] A known method for the measurement of chlorine ions using 0.01 N hydrochloric acid was used. In this method, however, the content of silver nitrate was indirectly determined by fixing the concentration of chlorine ions instead of measuring it. An experimental kit (OfficeAhn) for silver mirror reactions was used as Comparative Example 5.

[Table 6]

	Silver nitrate concentration (M)
Example 1	<0.001
Example 2	<0.001
Example 3	<0.001
Example 4	<0.001
Example 5	<0.001

(continued)

	Silver nitrate concentration (M)
Comparative Example 3	0.7
Comparative Example 4	0.9
Comparative Example 5	4.5

[0109] As can be seen from the results in Table 6, the amounts of silver nitrate formed in the plating solutions used in Examples 1-5 were below the limit of detection. The plating solutions used in Examples 1-5 were found to be highly stable during long-term storage before or after use because explosive silver nitrate was not produced. In contrast, silver nitrate was produced in the commercial silver plating solutions of Comparative Examples 3-4, which are currently used for silver plating, indicating that the concentration of silver nitrate may increase when the silver plating solutions are concentrated or stored for a long period of time. Finally, a large amount of silver nitrate was detected by the experimental kit for silver mirror reactions because the kit directly uses silver nitrate.

Claims

1. An electroless silver plating solution comprising a silver complex solution and a reducing agent solution wherein the silver complex solution comprises a silver carboxylate represented by Formula 1:

[Formula 1] R_1-COOAg

wherein R_1 is hydrogen, substituted or unsubstituted C_1-C_{22} alkyl, substituted or unsubstituted C_3-C_{30} cycloalkyl, substituted or unsubstituted C_6-C_{30} aralkyl, substituted or unsubstituted C_1-C_{30} heteroalkyl, substituted or unsubstituted C_2-C_{30} heterocycloalkyl or substituted or unsubstituted C_5-C_{30} heteroaralkyl, and the electroless silver plating is based on a silver mirror reaction between the silver complex solution and the reducing agent solution.

2. The electroless silver plating solution according to claim 1, wherein the silver complex solution further comprises a nitrogen-containing compound as a complexing agent and a solvent.

3. The electroless silver plating solution according to claim 2, wherein the nitrogen-containing compound is selected from the group consisting of ammonia, amines, quaternary ammonium salts, polyamines, and mixtures thereof.

4. The electroless silver plating solution according to claim 3, wherein the nitrogen-containing compound is an amine represented by Formula 2:

[Formula 2] $(R_2R_3R_4)N$

wherein R_2 to R_4 are the same as or different from each other and are each independently hydrogen, substituted or unsubstituted C_1-C_{20} alkyl, substituted or unsubstituted C_6-C_{30} aryl, substituted or unsubstituted C_3-C_{30} cycloalkyl, substituted or unsubstituted C_6-C_{30} aralkyl, substituted or unsubstituted C_1-C_{30} heteroalkyl, substituted or unsubstituted C_2-C_{30} heterocycloalkyl, substituted or unsubstituted C_5-C_{30} heteroaryl or substituted or unsubstituted C_5-C_{30} heteroaralkyl, or a quaternary ammonium salt compound represented by Formula 3:

[Formula 3] $(R_5R_6R_7R_8)N^+X$

wherein R_5 to R_8 are as defined for R_2 to R_4 in Formula 2 and X is F^-, Cl^-, Br^-, I^-, OH^-, hydrogen sulfate, bicarbonate, carbamate or perchlorate.

5. The electroless silver plating solution according to claim 2, wherein the nitrogen-containing compound is ammonia or an alkylamine.

6. The electroless silver plating solution according to claim 2, wherein the solvent is water, ethanol, ethylene glycol, glycerin or a mixed solvent thereof.

7. The electroless silver plating solution according to claim 2, wherein the complexing agent is present in a molar ratio 0.1-10.0 relative to the silver carboxylate.

8. The electroless silver plating solution according to claim 2, wherein the complexing agent binds to a silver ion of the silver carboxylate to form a complex ion.

9. The electroless silver plating solution according to claim 1, wherein the reducing agent solution comprises a reducing agent selected from the group consisting of glucose, hydrazine, hydroquinone, and derivatives thereof and a solvent.

10. The electroless silver plating solution according to claim 9, wherein the solvent is water, ethanol, ethylene glycol, glycerin or a mixed solvent thereof.

11. The electroless silver plating solution according to claim 10, wherein the solvent is a mixed solvent comprising 1 to 80% by weight of water.

12. The electroless silver plating solution according to claim 9, wherein the reducing agent solution further comprises one or more additives comprising an ammonium salt.

13. The electroless silver plating solution according to claim 12, wherein the ammonium salt is present in an amount of 0.01 to 10.0% by weight, based on the weight of the final plating solution.

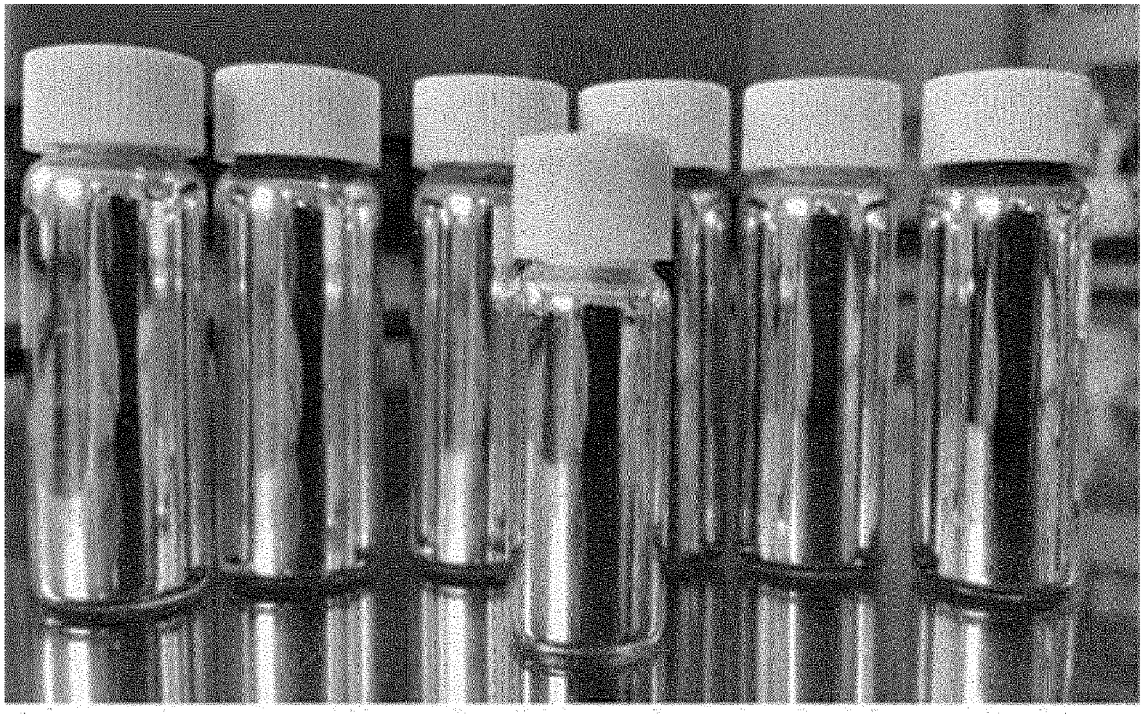
14. The electroless silver plating solution according to claim 1, wherein the silver carboxylate is a silver alkanoate.

15. The electroless silver plating solution according to claim 1, wherein the content of silver is 0.05 to 5.0% by weight, based on the weight of the final plating solution.

16. The electroless silver plating solution according to claim 1, wherein the reducing agent is present in a molar ratio of 0.1-5.0 relative to the silver carboxylate.

17. A silver-plated product manufactured by reaction with the silver plating solution according to any one of claims 1 to 16 at 5 to 50 °C.

[Fig. 1]

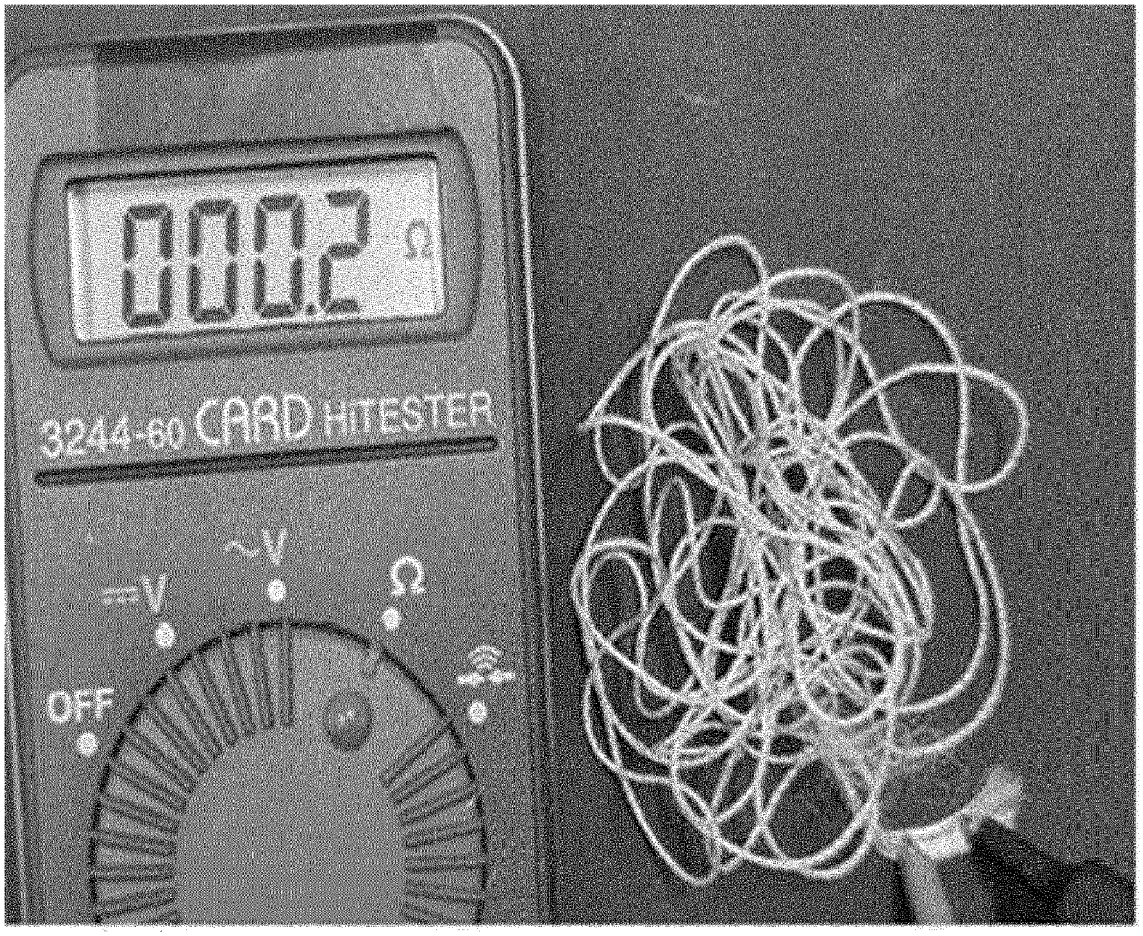


[Fig. 2]

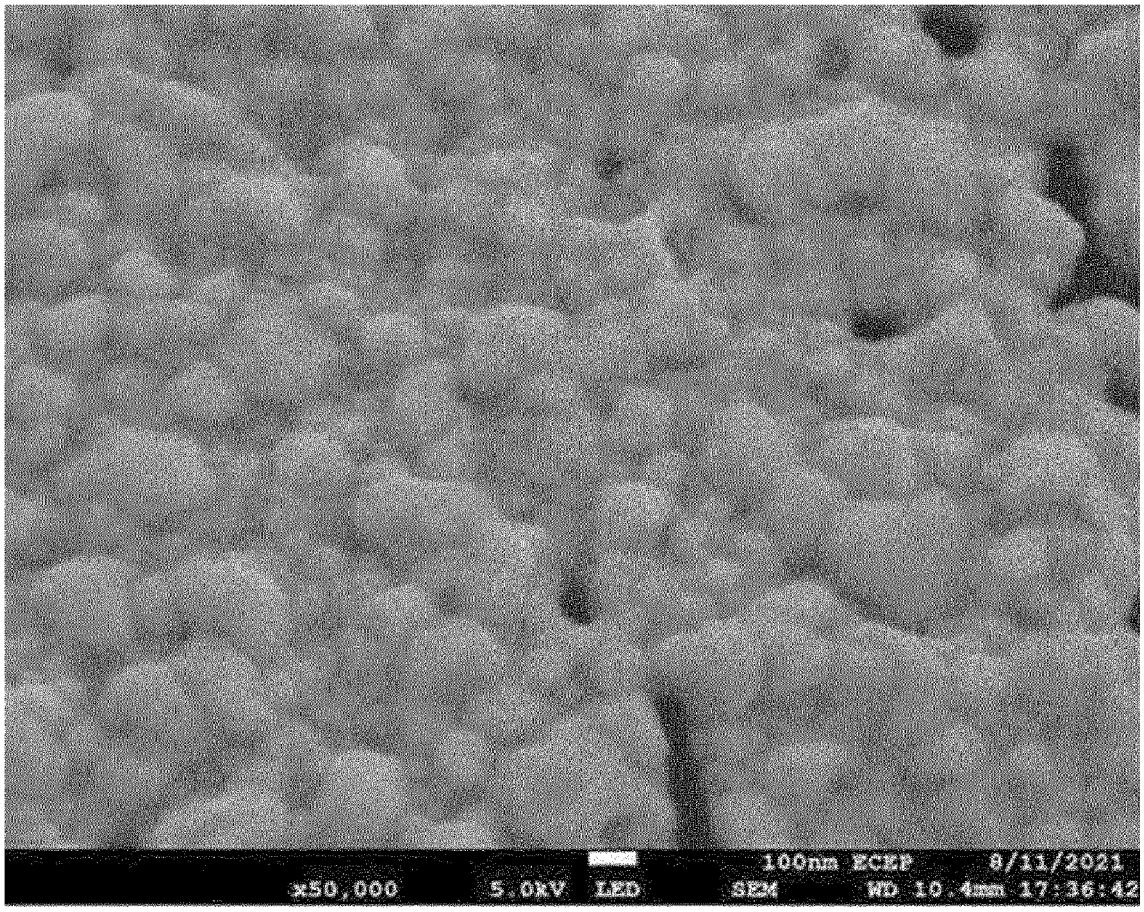
[Fig. 3]

[Fig. 4]

[Fig. 5]

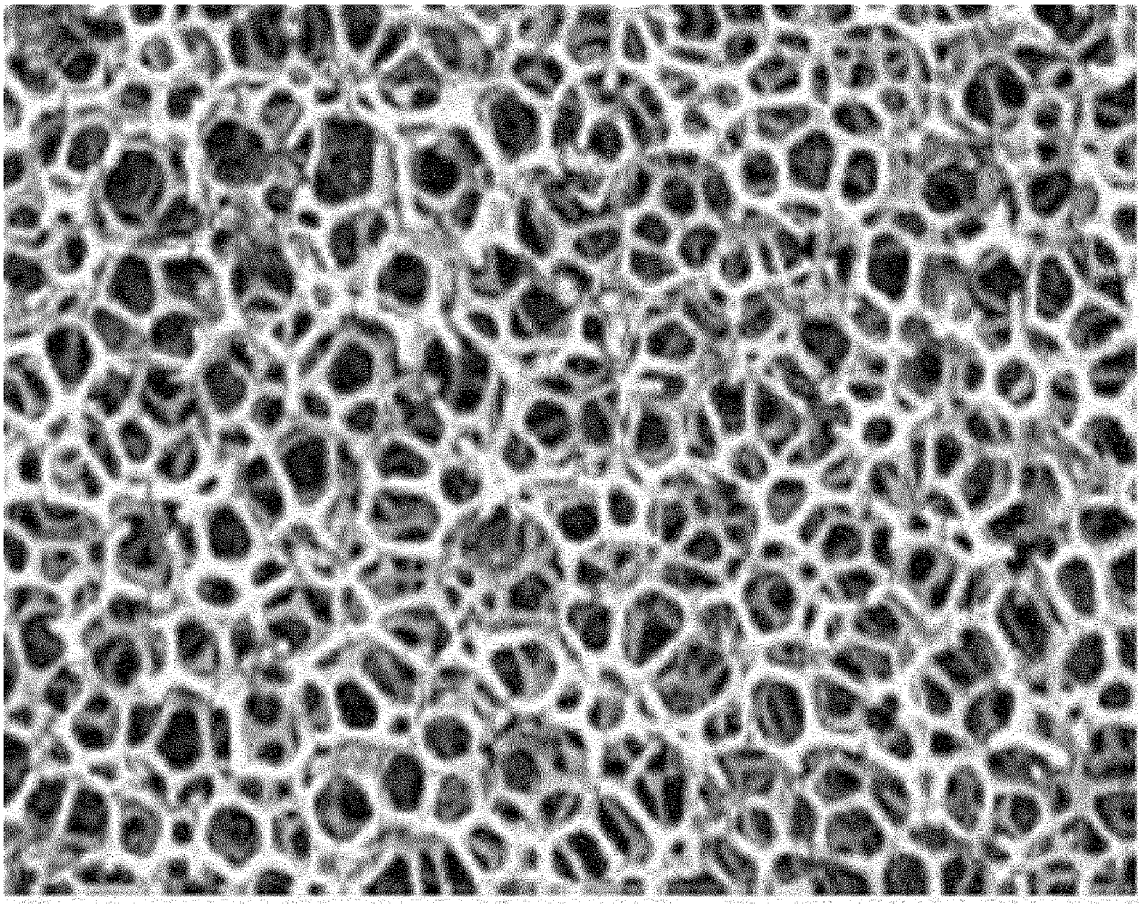


[Fig. 6]

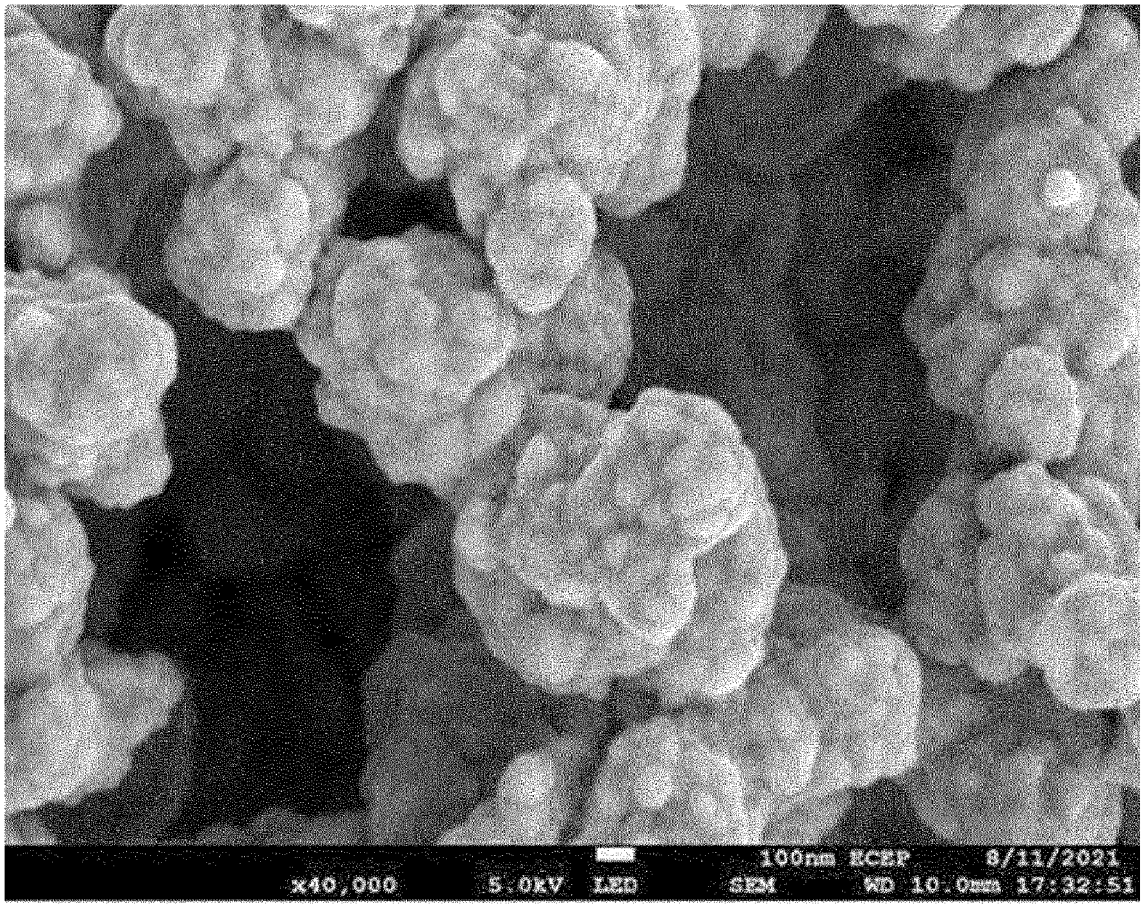


[Fig. 7]

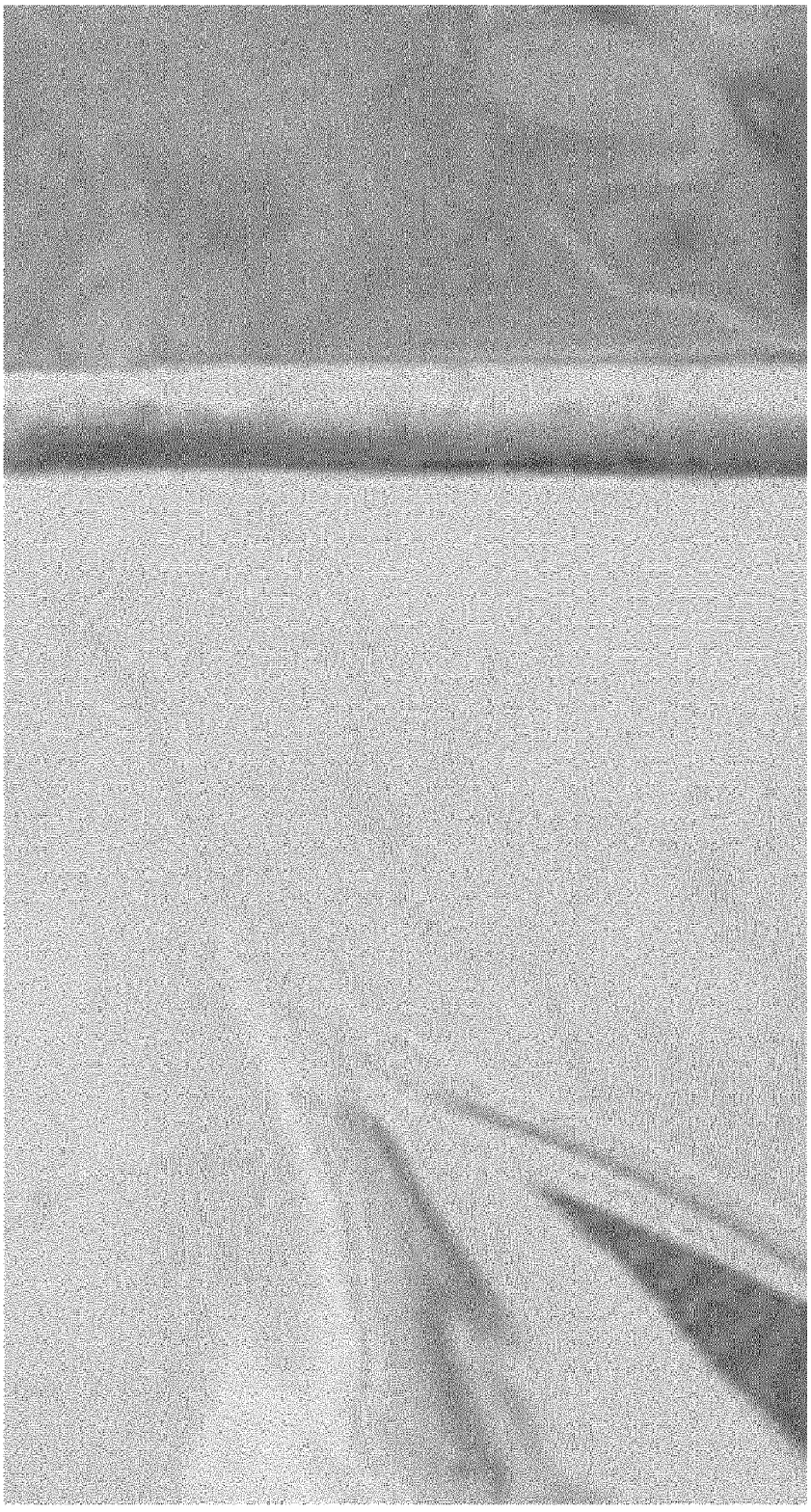
[Fig. 8]



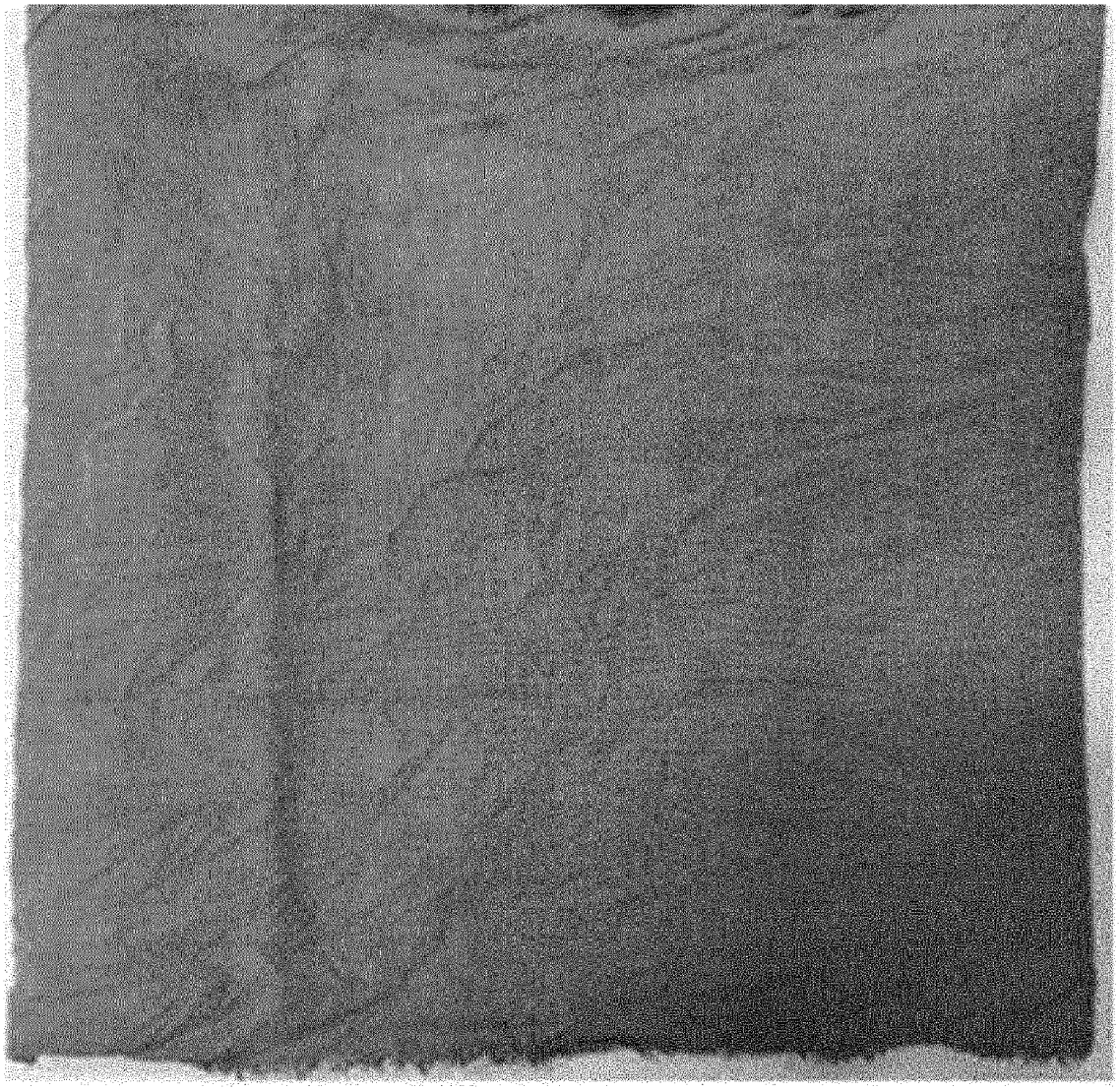
[Fig. 9]



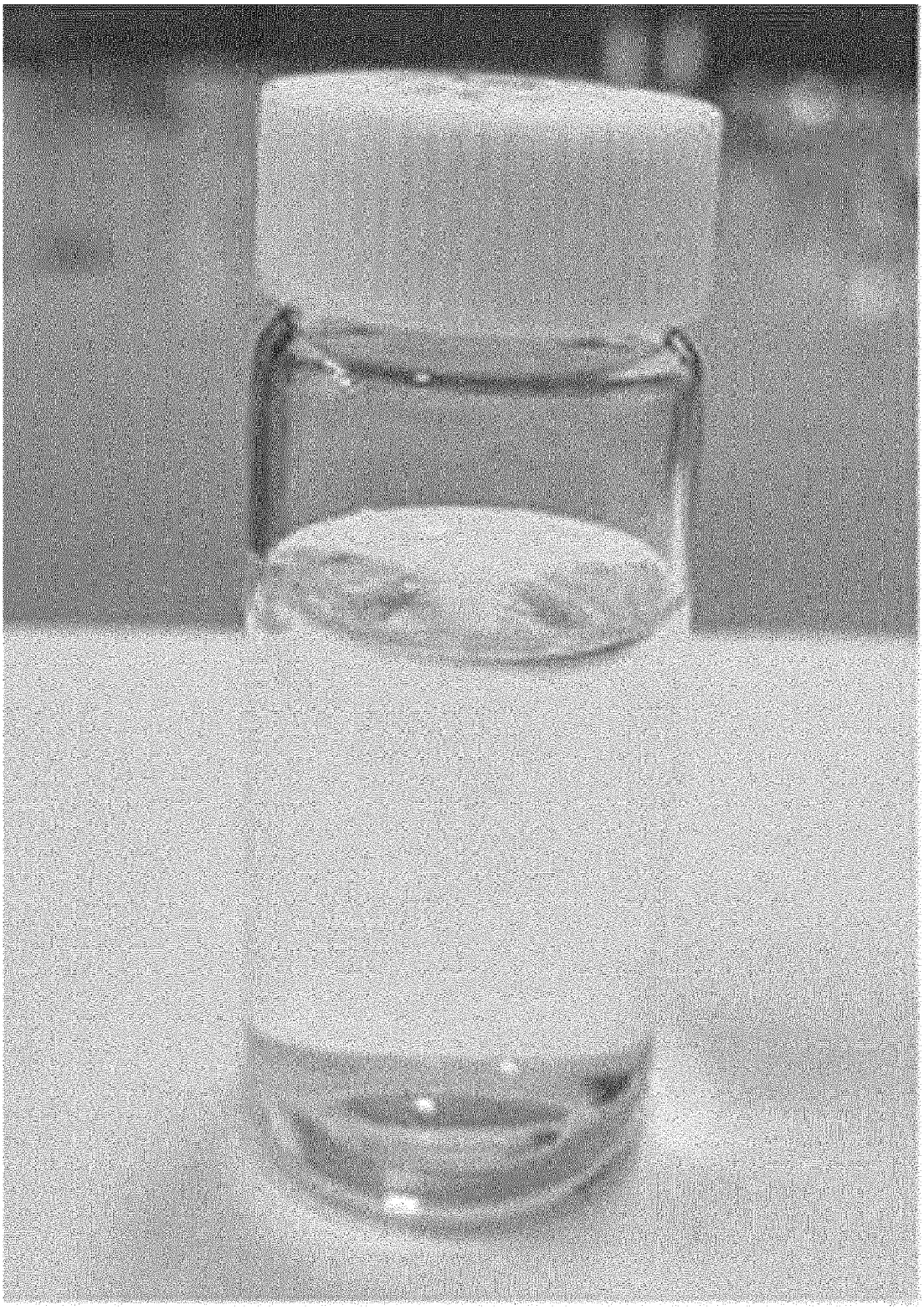
[Fig. 10]



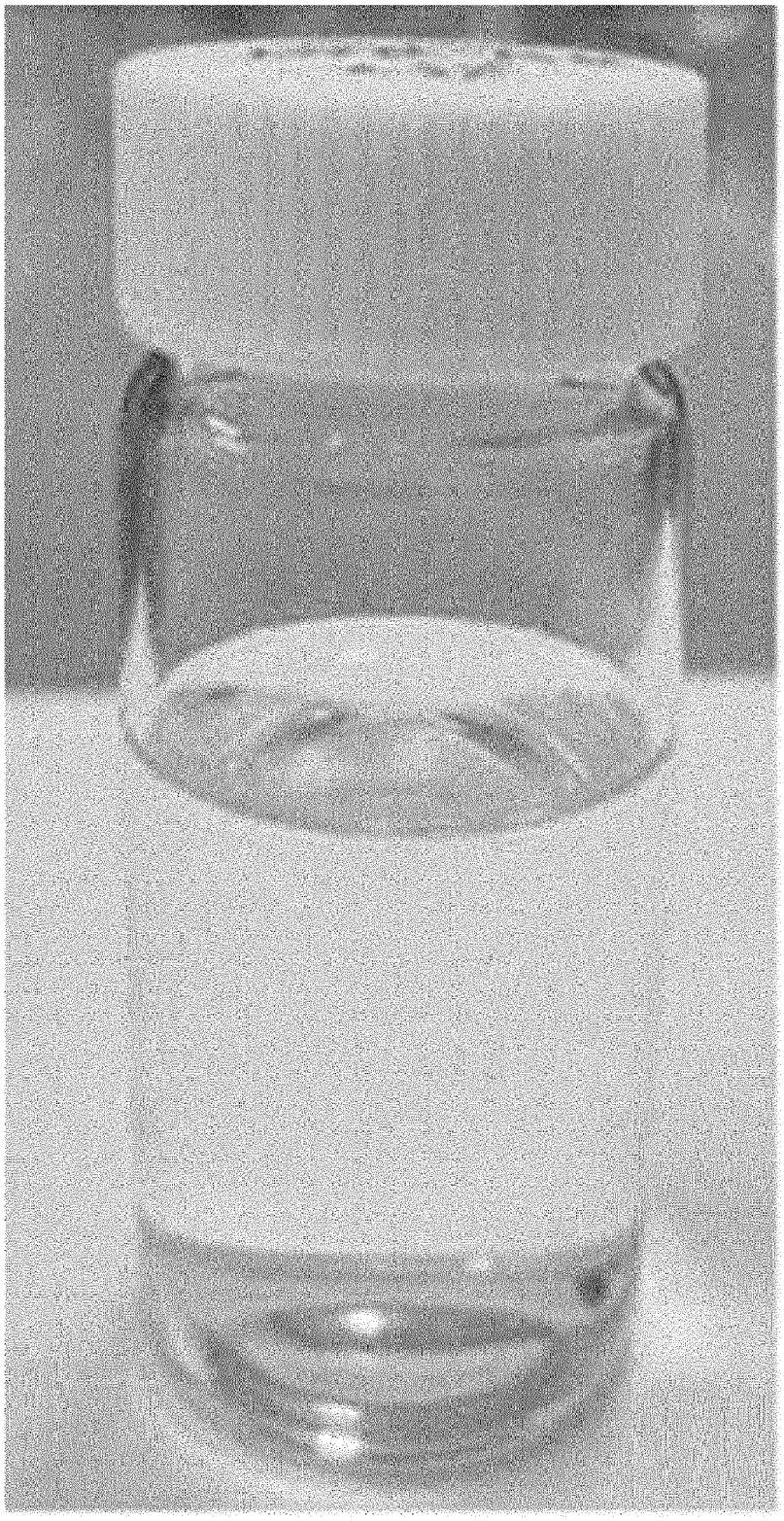
[Fig. 11]



[Fig. 12]



[Fig. 13]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2022/018390

A. CLASSIFICATION OF SUBJECT MATTER

C23C 18/44(2006.01)i; **C25D 3/46**(2006.01)i; **C23C 18/16**(2006.01)i; **C25D 5/54**(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)

C23C 18/44(2006.01); C01B 31/04(2006.01); C01B 31/08(2006.01); C09D 11/00(2006.01); C09D 11/52(2014.01)

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

Korean utility models and applications for utility models: IPC as above
Japanese utility models and applications for utility models: IPC as above

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

eKOMPASS (KIPO internal) & keywords: COOAg, 암모니아(ammonia), 착체(complexing), 은(Ag), 카르복실산(carboxylic acid), 무전해(electroless), 도금(plating)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR 10-2015-0063042 A (TOPPAN FORMS CO., LTD.) 08 June 2015 (2015-06-08) See paragraph [0110] and claim 1.	1-17
A	KR 10-2012-0118886 A (INKTEC CO., LTD.) 30 October 2012 (2012-10-30) See claims 1, 5, 9 and 11.	1-17
A	JP 2012-082444 A (C UYEMURA & CO., LTD.) 26 April 2012 (2012-04-26) See paragraphs [0010], [0016], [0018], [0032] and [0041].	1-17
A	KR 10-2006-0093789 A (ANCI CO., LTD.) 25 August 2006 (2006-08-25) See claims 1 and 6.	1-17
A	KR 10-2014-0113681 A (HENKEL IP & HOLDING GMBH) 24 September 2014 (2014-09-24) See claims 1 and 4.	1-17

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

* Special categories of cited documents:
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"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
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 March 2023	**06 March 2023**
Name and mailing address of the ISA/KR **Korean Intellectual Property Office** **Government Complex-Daejeon Building 4, 189 Cheongsa-ro, Seo-gu, Daejeon 35208** Facsimile No. **+82-42-481-8578**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2022/018390

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