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# (54) ELECTROLESS PLATING METHOD

(57) The present invention provides an electroless plating method capable of forming a plating film that is highly adhesive to a molded resin article while exhibiting high plating deposition performance without using harmful chromic acid. The electroless plating method for a resin material, includes (1) step 1: bringing a surface to be treated of the resin material into contact with a surface conditioner, (2) step 2: after step 1, bringing the surface to be treated of the resin material into contact with a pre-treatment composition, (3) step 3: after step 2, bringing the surface to be treated of the resin material into contact with a post-treatment solution containing an inorganic acid, (4) step 4: after step 3, bringing the surface to be treated of the resin material into contact with a catalyst-adding solution, and (5) step 5: after step 4, bringing the surface to be treated of the resin material into contact with an electroless plating solution, wherein the surface conditioner contains an ether-bond-containing solvent, and the pre-treatment composition contains 10 mg/L or more of manganese ions and 10 mg/L or more of monovalent silver ions.

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## Description

### Technical Field

**[0001]** The present invention relates to an electroless plating method.

### Background Art

**[0002]** Molded resin articles have been used in automobile parts, for example, for reducing the weight of automobiles. Resins used in molded resin articles for this purpose include, for example, ABS resin, PC/ABS resin, PPE resin, and polyamide resin. Such molded resin articles are plated with copper, nickel, or other metals to add a luxurious appearance or aesthetic: appeal. Additionally, a plating film such as a copper film has also been formed on a resin substrate as a method for forming a conductor circuit by imparting conductivity to such a resin substrate.

**[0003]** A typical method for forming a plating film on a resin material, such as a resin substrate or a molded resin article, includes performing etching treatment with chromic acid to roughen the surface of the resin material, optionally followed by neutralization and pre-dipping; adding an electroless plating catalyst using a colloid solution containing a tin compound and a palladium compound; performing activation treatment (accelerator treatment) for removing tin; and sequentially performing electroless plating and electroplating.

**[0004]** However, this method is harmful to the environment and the human body because of the use of chromic acid.

**[0005]** The following method for forming a plating film on a resin material is suggested; the method includes bringing a part to be plated into contact with an aqueous solution containing a metal activator species to perform etching, bringing the part into contact with a solution of a reducing agent capable of reducing the metal activator species, and bringing the part into contact with an electroless plating solution to perform metal plating (see PTL 1).

**[0006]** However, there is room to research the components of the activator species in the method according to PTL 1. The plating film formation in PTL 1 is also insufficient. It is difficult to form a plating film on the molded resin article, in particular, PC/ABS resin. Thus, a plating film cannot be sufficiently formed on the molded resin article, and the adhesion of the plating film to the molded resin article also becomes insufficient.

**[0007]** Thus, there is demand for the development of an electroless plating method capable of forming a plating film that is highly adhesive to a molded resin article while exhibiting high plating deposition performance, without the need for harmful chromic acid.

### Citation List

### Patent Literature

**[0008]** PTL 1: Patent No. 4198799

### Summary of Invention

### Technical Problem

**[0009]** The present invention has been made in view of the problems described above. An object of the invention is to provide an electroless plating method capable of forming a plating film that is highly adhesive to a molded resin article while exhibiting high plating deposition performance without using harmful chromic acid.

### Solution to Problem

**[0010]** The present inventors conducted extensive research to achieve the object, and found that the object can be achieved by an electroless plating method including the steps of bringing a surface to be treated of a resin material into contact with a surface conditioner, a pre-treatment composition, a post-treatment solution containing an inorganic acid, a catalyst-adding solution, and an electroless plating solution, wherein the surface conditioner contains an ether-bond-containing solvent, and the pre-treatment composition contains 10 mg/L or more of manganese ions and 10 mg/L or more of monovalent silver ions. The inventors then completed the present invention.

**[0011]** Specifically, the present invention relates to the following electroless plating method.

1. An electroless plating method for a resin material, comprising

   (1) step 1: bringing a surface to be treated of the resin material into contact with a surface conditioner,

(2) step 2: after step 1, bringing the surface to be treated of the resin material into contact with a pre-treatment composition,
(3) step 3: after step 2, bringing the surface to be treated of the resin material into contact with a post-treatment solution containing an inorganic acid,
(4) step 4: after step 3, bringing the surface to be treated of the resin material into contact with a catalyst-adding solution, and
(5) step 5: after step 4, bringing the surface to be treated of the resin material into contact with an electroless plating solution,

wherein

the surface conditioner contains an ether-bond-containing solvent, and
the pre-treatment composition contains 10 mg/L or more of manganese ions and 10 mg/L or more of monovalent silver ions.

2. The electroless plating method according to Item 1, wherein manganese of the manganese ions has a valence of 3 or more.

3. The electroless plating method according to Item 1 or 2, wherein the inorganic acid is at least one member selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, hydrofluoric acid, and boric acid.

4. The electroless plating method according to any one of Items 1 to 3, wherein the catalyst-adding solution contains 0.1 mg/L or more of a palladium compound and does not contain a tin compound.

5. The electroless plating method according to any one of Items 1 to 4, wherein the resin material is an alloy resin of a styrene-based resin and a polycarbonate (PC) resin.

## Advantageous Effects of Invention

**[0012]** The electroless plating method according to the present invention is capable of forming a plating film that is highly adhesive to a molded resin article while exhibiting high plating deposition performance without using harmful chromic acid.

## Description of Embodiments

**[0013]** The present invention is described below in detail.

### 1. Electroless Plating Method

**[0014]** The electroless plating method according to the present invention is an electroless plating method for a resin material, and comprises

(1) step 1: bringing a surface to be treated of the resin material into contact with a surface conditioner,
(2) step 2: after step 1, bringing the surface to be treated of the resin material into contact with a pre-treatment composition,
(3) step 3: after step 2, bringing the surface to be treated of the resin material into contact with a post-treatment solution containing an inorganic acid,
(4) step 4: after step 3, bringing the surface to be treated of the resin material into contact with a catalyst-adding solution, and
(5) step 5: after step 4, bringing the surface to be treated of the resin material into contact with an electroless plating solution,

wherein

the surface conditioner contains an ether-bond-containing solvent, and
the pre-treatment composition contains 10 mg/L or more of manganese ions and 10 mg/L or more of monovalent silver ions.

**[0015]** Because of steps 1 to 5 and the surface conditioner containing an ether-bond-containing solvent used in step 1, the electroless plating method according to the present invention can sufficiently form a plating film on a molded resin article, in particular, on a molded resin article of resins such as PC/ABS resin, on which it is difficult to form a plating film.

**[0016]** Because of the pre-treatment composition containing 10 mg/L or more of manganese ions and 10 mg/L or more of monovalent silver ions used in step 2, the electroless plating method according to the present invention can exert a high etching power on the surface to be treated of the resin material and sufficiently add a silver catalyst.

**[0017]** For example, a pre-treatment composition containing manganese ions and palladium ions, due to the presence of palladium ions, suffers a decrease in etching power of manganese ions. Additionally, a pre-treatment composition containing chromic acid and silver ions generates a precipitate of silver chromate ($Ag_2CrO_4$), which is an insoluble precipitate, in the composition, and this discharges silver ions out of the system, thereby resulting in insufficient addition of a catalyst.

**[0018]** In contrast, due to the presence of manganese ions and monovalent silver ions in the pre-treatment composition for use in step 2, bringing the surface to be treated of the resin material into contact with the pre-treatment composition allows silver to be adsorbed onto the surface to be treated of the resin material. Subsequently immersing the surface to be treated of the resin material in a post-treatment solution containing an inorganic acid allows the manganese residue to be removed. Subsequently immersing the surface to be treated of the resin material in a catalyst solution containing palladium ions allows silver to be replaced with palladium. Subsequently bringing the surface to be treated of the resin material into contact with an electroless plating solution allows a plating film to sufficiently form on the surface to be treated with excellent adhesion.

**[0019]** Specifically, the electroless plating method according to the present invention can form a plating film on molded resin articles on which it is difficult to form a plating film (e.g., PC/ABS resin), with the film highly adhered to the molded resin articles, exhibiting high plating deposition performance without using harmful chromic acid.

**[0020]** In the electroless plating method according to the present invention, the resin for forming a resin material that serves as an object to be treated is not particularly limited. The resin for forming a resin material for use can be various resin materials that are conventionally etched by using an acid mixture of chromic acid and sulfuric acid. Examples of resins for forming a resin material include styrene-based resins such as acrylonitrile-butadiene-styrene copolymer resin (ABS resin), resin in which the butadiene rubber component of ABS resin is replaced with an acrylic rubber component (AAS resin), and resin in which the butadiene rubber component of ABS resin is replaced with an ethylene-propylene rubber component (AES resin). For example, an alloy resin of the styrene-based resin and polycarbonate (PC) resin (e.g., an alloy resin with a PC resin content of about 30 to 70 mass%) is also preferable for use. In particular, an alloy resin of ABS resin and polycarbonate resin (PC/ABS resin), for example, an alloy resin of ABS resin and polycarbonate resin (PC/ABS resin) with a PC resin content of about 30 to 70 mass% is also preferable for use. Additionally, resins excellent in heat resistance and physical properties such as polyphenylene ether resin, polyphenylene oxide resin, polybutylene terephthalate (PBT) resin, polyphenylene sulfide (PPS) resin, and polyamide resin are also usable. The electroless plating method according to the present invention exhibits high plating deposition performance and can form a highly adhesive plating film on, among these resins, in particular, a PC/ABS resin, on which it is difficult to form a plating film.

**[0021]** The shape and size of the resin material are not particularly limited. The electroless plating method according to the present invention can form a plating film excellent in decorativeness and physical properties on a large resin material with a large surface area. Such large resin materials include automobile-related parts such as radiator grilles, hubcaps, small or medium-sized emblems, and door handles; exterior parts in the electrical and electronic fields; water faucet metal fittings used in water supply; and recreational machine-related products such as *pachinko* parts.

## Step 1

**[0022]** Step 1 is bringing the surface to be treated of a resin material into contact with a surface conditioner.

**[0023]** The surface conditioner for use in step 1 contains an ether-bond-containing solvent. The electroless plating method according to the present invention can sufficiently form a plating film on a molded resin article, in particular a molded resin article on which it is difficult to form a plating film (e.g., PC/ABS resin), by bringing the surface to be treated of the resin material into contact with the surface conditioner containing an ether-bond-containing solvent in step 1.

**[0024]** The ether-bond-containing solvent can be any solvent that has an ether bond in its molecule and that is usable as a solvent. Examples of such ether-bond-containing solvents include glycol ether solvents, cyclic ether solvents, and aromatic-ring-containing ether solvents.

**[0025]** Examples of glycol ether solvents include ethylene glycol, ethylene glycol monomethyl ether, propylene glycol monomethyl ether (PGME: also known as 1-methoxy-2-propanol), propylene glycol dimethyl ether, propylene glycol diethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol monomethyl ether, triethylene glycol monoethyl ether, methoxy methyl butanol, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, propylene glycol monoethyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether, propylene glycol monophenyl ether, diethylene glycol monoethyl ether, and diethylene glycol monoethyl ether acetate.

**[0026]** Examples of cyclic ether solvents include tetrahydrofuran, tetrahydropyran, and propylene carbonate.

**[0027]** Examples of aromatic-ring-containing ether solvents include diphenyl ether, and anisole (methylphenyl ether).

**[0028]** Of the ether-bond-containing solvents above, from the standpoint of more sufficiently forming a plating film on a molded resin article, ethylene glycol, ethylene glycol monobutyl ether, diethylene glycol monoethyl ether acetate, and propylene carbonate are preferable, and ethylene glycol monobutyl ether, diethylene glycol monoethyl ether acetate, and propylene carbonate are more preferable.

**[0029]** One kind of ether-bond-containing solvents may be used alone, or two or more kinds of ether-bond-containing solvents may be used in combination.

**[0030]** The amount of the ether-bond-containing solvent in the surface conditioner is not particularly limited. The amount of the ether-bond-containing solvent is preferably 5 g/L or more, more preferably 10 g/L or more, still more preferably 50 g/L or more, and particularly preferably 100 g/L or more. The amount of the ether-bond-containing solvent is also preferably 900 g/L or less, more preferably 850 g/L or less, still more preferably 500 g/L or less, and particularly preferably 300 g/L or less. A lower limit of the amount of the solvent within these ranges allows a plating film with higher adhesion to sufficiently form on a molded resin article. An upper limit of the amount of the solvent within these ranges provides a film appearance with better decorativeness.

**[0031]** The solvent in the surface conditioner is preferably dissolved in a solvent such as water. Specifically, the surface conditioner is preferably an aqueous solution (i.e., an ether-bond-containing solvent dissolved in water).

**[0032]** The surface conditioner may further contain other additives in addition to the ether-bond-containing solvent. These other additives include a surfactant.

**[0033]** The method for bringing the surface to be treated of the resin material into contact with the surface conditioner is not particularly limited and can be a known method. The method can be, for example, immersing the resin material in the surface conditioner, or spraying the surface to be treated of the resin material with the surface conditioner. Of these, from the standpoint of better contact efficiency, immersing the resin material in the surface conditioner is preferable.

**[0034]** The temperature of the surface conditioner in step 1 is not particularly limited and is preferably 20 to 100°C, more preferably 30 to 90°C, and still more preferably 40 to 80°C. A lower limit of the temperature of the surface conditioner within these ranges allows a highly adhesive plating film to more sufficiently form on a molded resin article. An upper limit of the temperature of the surface conditioner within these ranges provides a film appearance with better decorativeness.

**[0035]** The contact time of the surface conditioner with the surface to be treated of the resin material in step 1 is preferably 10 seconds to 60 minutes, more preferably 30 seconds to 30 minutes, and still more preferably 1 to 15 minutes. A lower limit of the contact time within these ranges allows a highly adhesive plating film to sufficiently form on a molded resin article. An upper limit of the contact time within these ranges provides a film appearance with better decorativeness.

**[0036]** Because of step 1 described above, the surface to be treated of the resin material can be brought into contact with the surface conditioner.

**[0037]** In the pre-treatment method of the present invention, a degreasing treatment may be performed before step 1 in order to remove smears on the surface to be treated of the resin material. The degreasing treatment is not particularly limited and can be performed according to a method known in the electroless plating field.

### Step 2

**[0038]** Step 2 is, after step 1, bringing the surface to be treated of the resin material into contact with a pre-treatment composition.

**[0039]** The pre-treatment composition for use in step 2 contains 10 mg/L or more of manganese ions and 10 mg/L or more of monovalent silver ions.

**[0040]** The specific amount of manganese ions and the specific amount of monovalent silver ions contained in the pre-treatment composition for use in step 2 allow high etching power to be exerted on the surface to be treated of the resin material and a silver catalyst to be sufficiently added.

**[0041]** For example, a pre-treatment composition containing manganese ions and palladium ions reduces the etching power of manganese ions due to the presence of palladium ions. A pre-treatment composition containing chromic acid and silver ions generates the precipitate of silver chromate ($Ag_2CrO_4$), which is an insoluble precipitate, in the composition, and this discharges silver ions outside the system, resulting in insufficient addition of a catalyst.

**[0042]** In contrast, due to the presence of manganese ions and monovalent silver ions in the pre-treatment composition according to the present invention, bringing the surface to be treated into contact with the pre-treatment composition allows silver to adsorb onto the surface. Subsequently immersing the surface to be treated in a post-treatment solution containing an inorganic acid allows the manganese residue to be removed. Subsequently immersing the surface to be treated in a catalyst solution containing palladium ions allows for silver to be replaced with palladium. Further bringing the surface to be treated into contact with an electroless plating solution allows for formation of a plating film well adhered to the surface.

**[0043]** Due to the presence of manganese ions and monovalent silver ions in the pre-treatment composition, etching of the surface to be treated of a resin substrate and addition of a silver catalyst both can be achieved simultaneously by bringing the surface to be treated into contact with the composition.

Manganese Ions

**[0044]** Manganese ions are not particularly limited as long as they have oxidizing power. Manganese of manganese ions preferably has a valence of 3 or more, more preferably 4 or more, and still more preferably 7. For example, manganese ions contained in the pre-treatment composition may be in the form of metal ions alone, such as trivalent manganese ions and quadrivalent manganese ions, or in the form of permanganate ions, which are septivalent manganese. Of these, from the standpoint of higher etching power, quadrivalent manganese ions and permanganate ions are preferable, and permanganate ions are more preferable. Manganese ions of divalent manganese have no oxidizing power, and the use thereof alone does not cause the surface of a resin material to be etched. However, such manganese ions may be used in combination with manganese ions of trivalent or higher-valent manganese.

**[0045]** One kind of manganese ions may be used alone or two or more kinds of manganese ions may be used in combination.

**[0046]** Manganate for adding manganese ions to the pre-treatment composition is not particularly limited, and includes manganese(II) sulfate, manganese(III) phosphate, manganese(IV) oxide, sodium permanganate(VII), and potassium permanganate(VII). Of these, from the standpoint of adding manganese ions that have higher etching power, manganese(III) phosphate, manganese(IV) oxide, sodium permanganate(VII), and potassium permanganate(VII) are preferable; and sodium permanganate(VII) and potassium permanganate(VII) are more preferable.

**[0047]** One kind of manganate may be used alone or two or more kinds of manganate may be used in combination.

**[0048]** The pre-treatment composition contains manganese ions in an amount of 10 mg/L or more. An amount of manganese ions of less than 10 mg/L leads to insufficient etching of a resin material, reducing the adhesion of the film formed by electroless plating. The amount of manganese ions is preferably 10 mg/L to 100 g/L, more preferably 100 mg/L to 50 g/L, still more preferably 0.2 g/L to 30 g/L, particularly preferably 0.5 g/L to 15 g/L, and most preferably 0.5 g/L to 10 g/L. Setting the lower limit of the amount of manganese ions within these ranges further improves the etching power of the pre-treatment composition. Setting the upper limit of the amount of manganese ions within these ranges further reduces the generation of the precipitate of manganese dioxide in the pre-treatment composition and further improves bath stability.

Silver Ions

**[0049]** The silver ions contained in the pre-treatment composition are monovalent silver ions. A silver salt for adding monovalent silver ions is not particularly limited as long as the silver salt can add monovalent silver ions that are stable in a bath when dissolved in the pre-treatment composition, and as long as the counterions that form the silver salt do not have an adverse effect on manganese ions. Specifically, such silver salts include silver(I) sulfate, silver(I) nitrate, and silver(I) oxide. Of these, from the standpoint of high solubility and convenience in industrial application, silver(I) nitrate is preferable. Silver(I) sulfate is also preferable because silver(I) sulfate leads to higher deposition performance in plating and higher resistance to decreases in adhesion of the plating film even on resin materials formed of a resin such as a polymer alloy of a styrene based-resin with a polycarbonate (PC) resin, on which it is hard to form a plating deposition.

**[0050]** One kind of such silver salts may be used alone, or two or more kinds of silver salts may be used in combination.

**[0051]** The pre-treatment composition contains monovalent silver ions in an amount of 10 mg/L or more. An amount of monovalent silver ions of less than 10 mg/L leads to insufficient deposition of electroless plating. The amount of monovalent silver ions is preferably 10 mg/L to 20 g/L, more preferably 50 mg/L to 15 g/L, and still more preferably 100 mg/L to 10 g/L. Setting the lower limit of the amount of monovalent silver ions within these ranges allows a sufficient amount of a silver catalyst to adsorb on the surface of a resin material and causes an electroless plating film to more sufficiently deposit on the surface. Although the amount of monovalent silver ions beyond the upper limits described above would not have an adverse effect, setting the upper limit as described above can reduce the amount of the silver salt for use, thereby decreasing cost.

**[0052]** Silver ions for use may be monovalent silver obtained by placing metal silver in an acidic manganese bath, and dissolving it. The acid for forming an acidic manganese bath is not particularly limited, and may be an inorganic acid or an organic sulfonic acid.

**[0053]** The inorganic acid includes sulfuric acid, phosphoric acid, nitric acid, hydrochloric acid, hydrofluoric acid, and boric acid. Of these, from the standpoint of excellence in effluent treatment, sulfuric acid and phosphoric acid are preferable, and sulfuric acid is more preferable.

**[0054]** The organic sulfonic acid includes $C_{1-5}$ aliphatic sulfonic acids, such as methanesulfonic acid, ethanesulfonic acid, propanesulfonic acid, and pentanesulfonic acid; and aromatic sulfonic acids, such as toluenesulfonic acid, pyridinesulfonic acid, and phenolsulfonic acid. Of these, from the standpoint of excellent bath stability of the pre-treatment composition, $C_{1-5}$ aliphatic sulfonic acids are preferable.

**[0055]** One kind of such acids may be used alone, or two or more kinds of acids may be used in combination.

**[0056]** The acid concentration of the pre-treatment composition is not particularly limited; for example, the pre-treatment composition has a total acid concentration of preferably 100 to 1800 g/L, and more preferably 800 to 1700 g/L.

### Other Component

**[0057]** The pre-treatment composition may contain a high-molecular compound in addition to the manganese ions and the silver ions. The type of the high-molecular compound is not particularly limited; from the standpoint of facilitating plating deposition, a cationic polymer may preferably be used. The amount of the high-molecular compound is preferably 0.01 to 100 g/L, and more preferably 0.1 to 10 g/L.

### Solvent

**[0058]** The manganese ions, the silver ions, and optionally added other components of the pre-treatment composition are preferably contained in a solvent. The solvent is not particularly limited, and includes water, an alcohol, and a mixture solvent of water and an alcohol.

**[0059]** The solvent is preferably water from the standpoint of its excellent safety. Specifically, the pre-treatment composition according to the present invention is preferably an aqueous solution.

**[0060]** The alcohol is not particularly limited, and a known alcohol, such as ethanol, may be used.

**[0061]** A mixture solvent of water and an alcohol for use preferably has a low alcohol concentration. Specifically, the alcohol concentration is preferably about 1 to 30 mass%.

**[0062]** The pre-treatment composition is preferably acidic. Due to the acidity of the pre-treatment composition, etching treatment on a resin material is more sufficiently performed. The pre-treatment composition preferably has a pH of 2 or less, and more preferably 1 or less.

**[0063]** The method for bringing the surface to be treated of a resin material into contact with the pre-treatment composition is not particularly limited. The surface of a resin material may be brought into contact with the pre-treatment composition by a known method. Such a method includes immersing a resin material in a pre-treatment composition, and spraying the surface to be treated of a resin material with a pre-treatment composition. Of these, from the standpoint of higher contact efficiency, immersing a resin material in a pre-treatment composition is preferable.

**[0064]** The temperature of the pre-treatment composition in step 2 is not particularly limited, and is preferably 30 to 100°C, more preferably 40 to 90°C, and still more preferably 50 to 80°C. Setting the lower limit of the temperature of the pre-treatment composition within these ranges ensures more sufficient etching of the resin material surface and addition of a catalyst. Setting the upper limit of the temperature of the pre-treatment composition within these ranges provides film appearance with much better decorativeness.

**[0065]** The contact time during which the pre-treatment composition is in contact with the surface to be treated of a resin material in step 2 is preferably 3 to 60 minutes, more preferably 5 to 50 minutes, and still more preferably 10 to 40 minutes. Setting the lower limit of the contact time within these ranges ensures more sufficient etching of the resin material surface and addition of a catalyst. Setting the upper limit of the contact time within these ranges provides film appearance with much better decorativeness.

**[0066]** The use of a chromic acid-sulfuric acid mixture, which is related art, leads to immediate generation of a precipitate of silver chromate ($Ag_2CrO_4$) when monovalent silver ions are added to a bath; this hinders silver from stably existing as ions in the pre-treatment composition. Thus, when a chromic acid-sulfuric acid mixture, which is related art, is used, it is hard to use a pre-treatment composition containing silver ions, unlike step 2 of the electroless plating method according to the present invention.

**[0067]** Because of step 2 described above, the surface to be treated of the resin material is brought into contact with the pre-treatment composition, and the surface to be treated is treated.

### Step 3

**[0068]** Step 3 is, after step 2, bringing the surface to be treated of the resin material into contact with a post-treatment solution containing an inorganic acid. Because the electroless plating method includes step 3 after step 2, manganese adhered to the surface of the resin material is removed.

**[0069]** The inorganic acid is not particularly limited, and examples include hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, hydrofluoric acid, and boric acid. Of these, from the standpoint of excellent manganese removability, hydrochloric acid is preferable.

**[0070]** One kind of such inorganic acids may be used alone, or two or more kinds of inorganic acids may be used in combination.

**[0071]** The amount of the inorganic acid in the post-treatment solution is not particularly limited, and is preferably 1 to 1000 g/L, more preferably 5 to 750 g/L, and more preferably 10 to 500 g/L.

**[0072]** The post-treatment method is not particularly limited. For example, a resin material that has been pretreated in step 2 may be immersed in the post-treatment solution at a liquid temperature of about 15 to 50°C for about 1 to 10 minutes. This post-treatment can further improve the deposition performance and appearance of the formed plating film.

**[0073]** Because of step 3 described above, the surface to be treated of the resin material is brought into contact with the post-treatment solution containing an inorganic acid.

## Step 4

**[0074]** Step 4 is, after step 3, bringing the surface to be treated of the resin material into contact with a catalyst-adding solution. Because of step 4, a catalyst is added to the surface of the resin material.

**[0075]** The catalyst-adding solution for use can be a known catalyst-adding solution typically used in adding a catalyst in electroless plating. The catalyst-adding solution can be, for example, a catalyst-adding solution containing a catalyst metal-containing compound.

**[0076]** The catalyst metal-containing compound can be any catalyst metal-containing compound that can be used in electroless plating. Examples include palladium compounds, and platinum compounds. Of these, from the standpoint of the simplicity of forming an electroless plating film on a resin material, palladium compounds are preferable.

**[0077]** The palladium compounds are preferably those that easily dissociate in water to release palladium ions, such as palladium chloride ($PdCl_2$), and palladium sulfate ($PdSO_4$).

**[0078]** The palladium in the catalyst-adding solution is preferably present in the form of palladium ions (i.e., being ions), and the palladium more preferably has a valence of +2.

**[0079]** The lower limit of the amount of the palladium compound in the catalyst-adding solution is preferably 0.01 mg/L or more, more preferably 0.1 mg/L or more, still more preferably 1 mg/L or more, and particularly preferably 10 mg/L or more. The upper limit of the amount of the palladium compound is preferably 2000 mg/L, more preferably 0.05 to 1500 mg/L, preferably 0.1 to 1000 mg/L or less, more preferably 1500 mg/L or less, still more preferably 1000 mg/L or less, and particularly preferably 750 mg/L or less.

**[0080]** The catalyst-adding solution may contain a tin compound. The tin compound is preferably a stannous compound, and such stannous compounds include those that easily dissociate in water to release stannous ions. Examples of stannous compounds include stannous chloride, and stannous sulfate.

**[0081]** In the electroless plating method according to the present invention, step 4, unlike the traditional catalyst-adding step, does not require the use of a palladium-tin colloid solution, and the catalyst-adding solution is preferably free of a tin compound. A catalyst-adding solution free of a tin compound eliminates the need for an activation treatment (accelerator treatment) step for removing tin and thus shortens the step of performing electroless plating.

**[0082]** Due to the palladium ions added by replacing silver through substitution reaction, the catalyst-adding solution also limits the adsorption of the catalyst onto the polycarbonate resin in a double-shot molding article of ABS resin and polycarbonate resin or a double-shot molding article of PC/ABS resin and polycarbonate resin, compared with a palladium catalyst in metal form such as palladium-tin colloid. Thus, the catalyst-adding solution is suitable for use in selective plating of these double-shot molding articles. Additionally, the adsorption of the catalyst onto the surface of a jig is reduced, and the precipitation of the plating film on the surface of a jig is also reduced. This reduces unevenness of the electroless plating film on the surface of a resin material, which occurs when the electroless plating film is formed by repeatedly using a jig because a precipitated plating film on the surface of the jig is peeled off in the form of particles and taken in by the electroless plating film on the surface of the resin material in each step. From the viewpoint above, the catalyst-adding solution preferably contains 0.1 mg/L or more of a palladium compound and contains no tin compound.

**[0083]** The method for bringing the surface to be treated of the resin material into contact with the catalyst-adding solution is not particularly limited, and can be a known method. The method can be, for example, immersing the resin material in the catalyst-adding solution, or spraying the surface to be treated of the resin material with the catalyst-adding solution. Of these, from the standpoint of better contact efficiency, immersing the resin material in the catalyst-adding solution is preferable.

**[0084]** The temperature of the catalyst-adding solution in step 4 is not particularly limited and is preferably 30 to 90°C, more preferably 40 to 80°C, and still more preferably 50 to 70°C.

**[0085]** The contact time during which the catalyst-adding solution is in contact with the surface to be treated of the resin material in step 4 is not particularly limited and may be about 1 to 10 minutes.

**[0086]** Because of step 4 described above, the surface to be treated of the resin material can be brought into contact with the catalyst-adding solution, and the catalyst is added to the surface to be treated of the resin material.

Step 5

**[0087]** Step 5 is, after step 4, bringing the surface to be treated of the resin material into contact with an electroless plating solution.

**[0088]** The method for bringing the surface to be treated of the resin material into contact with an electroless plating solution is not particularly limited. The surface to be treated of the resin material may be brought into contact with an electroless plating solution by a known method. From the standpoint of much higher contact efficiency, the method is preferably immersing the surface to be treated of a resin material in an electroless plating solution.

**[0089]** The electroless plating solution is not particularly limited, and a known autocatalytic electroless plating solution may be used. The electroless plating solution includes electroless nickel plating solutions, electroless copper plating solutions, electroless cobalt plating solutions, electroless nickel-cobalt alloy plating solutions, and electroless gold plating solutions.

**[0090]** The electroless nickel plating solutions can be, for example, a plating solution containing nickel sulfate, a hydrate thereof, or the like. The electroless copper plating solutions can be, for example, a plating solution containing cupric sulfate, a hydrate thereof, or the like.

**[0091]** From the standpoint of increasing plating deposition performance, the electroless plating solution may contain a reducing agent. The reducing agent is not particularly limited, and the reducing agent includes dimethylamine borane, formalin, glyoxylic acid, tetrahydroboric acid, hydrazine, hypophosphite, erythorbic acid, ascorbic acid, hydroxylamine sulfate, hydrogen peroxide, and glucose. Of these, from the standpoint of catalytic activity on silver and much higher plating deposition performance, dimethylamine borane, formalin, glyoxylic acid, tetrahydroboric acid, and hydrazine are preferable.

**[0092]** One kind of such reducing agents may be used alone, or two or more kinds of reducing agents may be used in combination.

**[0093]** The amount of the reducing agent in the electroless plating solution is not particularly limited, and is preferably 0.01 to 100 g/L, more preferably 0.1 to 50 g/L, still more preferably 1 to 30 g/L, and particularly preferably 5 to 20 g/L. Setting the lower limit of the amount of the reducing agent within these ranges further improves plating deposition performance, and setting the upper limit of the amount of the reducing agent within these ranges further improves the stability of the electroless plating bath.

**[0094]** From the standpoint of increasing the precipitation stability of the plating solution, the electroless plating solution may contain an organic acid complexing agent. The organic acid complexing agent is not particularly limited, and includes formic acid, oxalic acid, glycolic acid, tartaric acid, citric acid, maleic acid, acetic acid, propionic acid, malonic acid, succinic acid, lactic acid, malic acid, gluconic acid, glycine, alanine, aspartic acid, glutamic acid, iminodiacetic acid, nitrilotriacetic acid, fumaric acid, and salts thereof. Of these, from the standpoint of much higher plating deposition performance, formic acid, oxalic acid, glycolic acid, tartaric acid, citric acid, maleic acid, or a salt thereof is preferable.

**[0095]** One kind of such organic acid complexing agents may be used alone, or two or more kinds of organic acid complexing agents may be used in combination.

**[0096]** The concentration of the organic acid complexing agent in the electroless plating solution is not particularly limited, and is preferably 0.1 to 500 g/L, more preferably 1 to 100 g/L, and still more preferably 2 to 50 g/L.

**[0097]** From the standpoint of improving plating deposition performance, the electroless plating solution may contain an alkaline compound. Examples of alkaline compounds include sodium hydroxide, potassium hydroxide, and ammonia.

**[0098]** One kind of such alkaline compounds may be used alone, or two or more kinds of such alkaline compounds may be used in combination.

**[0099]** The concentration of the alkaline compound in the electroless plating solution is not particularly limited, and is preferably 1 to 50 g/L, and more preferably 5 to 15 g/L.

**[0100]** From the standpoint of improving plating deposition performance, the electroless plating solution may contain a complexing agent.

**[0101]** The complexing agent is not particularly limited and can be a known complexing agent used in electroless plating solutions. Examples of such complexing agents include ethylenediamine diacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, ammonium salts thereof, potassium salts thereof, sodium salts thereof, amino polycarboxylic acids such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid, sodium salts thereof, potassium salts thereof, and ammonium salts thereof.

**[0102]** One kind of such complexing agents may be used alone, or two or more kinds of such complexing agents may be used in combination.

**[0103]** The concentration of the complexing agent in the electroless plating solution is not particularly limited, and is preferably 1 to 50 g/L, more preferably 5 to 40 g/L, and still more preferably 10 to 30 g/L.

**[0104]** The conditions under which the surface to be treated of the resin material is brought into contact with the electroless plating solution are not particularly limited; for example, when a resin material is immersed in the electroless plating solution, the liquid temperature of the electroless plating solution can be about 20 to 70°C, and the immersion time can be about 3 to 30 minutes.

**[0105]** In the electroless plating method according to the present invention, step 5 may optionally be performed 2 or more times. Two layers or more of the electroless plating film is formed by performing step 5 two or more times.

**[0106]** Because of step 5 described above, the surface to be treated of the resin material is brought into contact with the electroless plating solution, and electroless plating is formed on the surface to be treated of the resin material.

**[0107]** The electroless plating method according to the present invention may further include, after step 5, an electroplating step.

**[0108]** The electroplating step may include optionally performing an activation treatment with an aqueous solution, such as of an acid or an alkali after step 5, and then immersing the resin material in an electroplating solution to perform electroplating.

**[0109]** The electroplating solution is not particularly limited, and can be suitably selected from known electroplating solutions according to the purpose.

**[0110]** The electroplating method is not particularly limited. For example, the resin material on which an electroless plating film has been formed in step 5 may be immersed in an activation treatment solution at a liquid temperature of about 15 to 50°C at a current density of about 0.1 to 10 A/dm$^2$ for about a few seconds to 10 minutes.

## Examples

**[0111]** The following describes the present invention in more detail with reference to Examples and Comparative Examples. However, the present invention is not limited to these Examples.

### Preparation of Electroless Plating Film

**[0112]** A flat plate (10 cm × 5 cm × 0.3 cm, surface area: about 1 dm$^2$) of ABS resin (manufactured by Techno-UMG Co., Ltd., registered trade name: ABS3001M) and a flat plate (10 cm × 5 cm × 0.3 cm, surface area: about 1 dm$^2$) of PC/ABS resin (manufactured by Techno-UMG Co., Ltd., trade name: TC25M) were prepared as a resin material (an object to be plated), and an electroless plating film was formed in accordance with the following method.

**[0113]** First, the resin material was immersed in an alkaline degreasing solution (manufactured by Okuno Chemical Industries Co., Ltd, Ace Clean A-220 bath) at 40°C for 5 minutes, and washed with water, thereby preparing a test specimen.

**[0114]** Subsequently, in accordance with the formulations shown in Table 1, the surface conditioners, pre-treatment compositions, post-treatment solutions, catalyst-adding solutions, and electroless plating solutions for use in the Examples and Comparative Examples were prepared. These solutions were prepared by adding additives to water (solvent) according to the formulations shown in Table 1 and stirring the mixture.

**[0115]** The test specimen was sequentially subjected to step 1 to step 5 under the following conditions by using the thusprepared solutions under the following conditions to add electroless plating to the specimen. In Comparative Example 1, step 1 was not performed. In Comparative Example 5, step 3 was not performed.

#### Step 1

**[0116]** Immersion in a surface conditioner: immersion temperature of 55°C, immersion time of 3 minutes

#### Step 2

**[0117]** Immersion in a pre-treatment composition: immersion temperature of 75°C, immersion time of 20 minutes

#### Step 3

**[0118]** Immersion in a post-treatment solution: immersion temperature of 40°C, immersion time of 1 minute

#### Step 4

**[0119]** Immersion in a catalyst-adding solution: immersion temperature of 60°C, immersion time of 3 minutes

Step 5

**[0120]** Immersion in an electroless plating solution: immersion temperature of 35°C, immersion time of 5 minutes

**[0121]** The deposit percentage and adhesion of the plating films formed from the resin materials treated with electroless plating solutions by the method above in the Examples and Comparative Examples were evaluated in accordance with the following procedures.

(1) Deposit Percentage

**[0122]** The percentage of the area of the electroless plating film on the surface of the resin material was evaluated as a deposit percentage. A full coverage of the surface of the resin material was taken as a deposit percentage of 100%.

(2) Peel Strength Measurement

**[0123]** The resin material having an electroless plating film formed thereon was immersed in a copper sulfate plating bath, and subjected to electroplating treatment at a current density of 3 A/dm$^2$ at a temperature of 25°C for 120 minutes to form a copper plating film, thereby preparing a sample. The sample was dried at 80°C for 120 minutes and allowed to stand until being cooled to room temperature. Subsequently, a 10-mm-width cut was made on the plating film, and the plating film was pulled in a direction perpendicular to the surface of the resin material with a tensile tester (manufactured by Shimadzu Corporation, autograph AGS-J 1kN), thereby measuring peel strength.

**[0124]** Table 1 shows the results.

Table 1

| | | Example 1 | Example 2 | Example 3 | Example 4 | Example 5 | Example 6 | Example 7 | Example 8 | Example 9 | Example 10 | Example 11 | Example 12 | Comparative Example 1 | Comparative Example 2 | Comparative Example 3 | Comparative Example 4 | Comparative Example 5 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Step 1 Surface Conditioner | Ethylene Glycol Monobutyl Ether (g/L) | 150 | 0 | 0 | 0 | 7 | 3 | 50 | 10 | 10 | 0 | 50 | 10 | — | 0 | 0 | 7 | 3 |
| | Propylene Carbonate (g/L) | 0 | 214 | 0 | 100 | 150 | 150 | 50 | 50 | 50 | 100 | 50 | 50 | — | 0 | 100 | 150 | 150 |
| | Diethylene Glycol Monoethyl Ether Acetate (g/L) | 0 | 0 | 220 | 20 | 0 | 10 | 50 | 100 | 100 | 20 | 50 | 100 | — | 220 | 20 | 0 | 10 |
| Step 2 Pre-treatment Composition | Manganese(II) Sulfate (g/L) | 0 | 20 | 0 | 100 | 0 | 5 | 15 | 10 | 10 | 100 | 15 | 10 | 0 | 0 | 100 | 0 | 5 |
| | Manganese(Ⅲ) Phosphate (g/L) | 0 | 30 | 0.04 | 0 | 0 | 0 | 2 | 8 | 8 | 0 | 2 | 8 | 0 | 0.02 | 0 | 0 | 0 |
| | Manganese(IV) Oxide (g/L) | 0 | 0 | 0 | 0 | 2 | 1 | 0 | 0.1 | 0.1 | 0 | 0 | 0.1 | 0 | 0 | 0 | 2 | 1 |
| | Sodium(VII) Permanganate (g/L) | 35 | 0 | 0 | 1 | 2 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 35 | 0 | 1 | 2 | 0 |
| | Sulfuric Acid (g/L) | 1100 | 100 | 0 | 780 | 200 | 200 | 780 | 0 | 0 | 780 | 780 | 0 | 1100 | 0 | 780 | 200 | 200 |
| | Phosphoric Acid (g/L) | 200 | 0 | 780 | 200 | 780 | 200 | 200 | 0 | 0 | 200 | 200 | 0 | 200 | 780 | 200 | 780 | 200 |
| | Methanesulfonic Acid (g/L) | 0 | 1000 | 380 | 200 | 200 | 780 | 200 | 1000 | 100 | 200 | 200 | 1000 | 0 | 380 | 200 | 200 | 780 |
| | Silver Nitrate (g/L) | 3.4 | 5 | 0.02 | 0 | 0 | 0 | 5 | 10 | 10 | 0 | 5 | 10 | 3.4 | 0.02 | 0 | 0 | 0 |
| | Silver Sulfate (g/L) | 0 | 0 | 0 | 2.4 | 1.2 | 0.2 | 0.2 | 1.2 | 1.2 | 2.4 | 0.2 | 1.2 | 0 | 0 | 0.01 | 1.2 | 0.2 |
| | Manganese Ion Content (mg/L) | 13548 | 17093 | 13 | 36771 | 2038 | 2451 | 6112 | 6319 | 6319 | 36771 | 6112 | 6319 | 13548 | 6 | 36771 | 2038 | 2451 |
| | Ag(I) Ion Content (mg/L) | 2160 | 3175 | 13 | 1661 | 831 | 138 | 3313 | 7181 | 7181 | 1661 | 3313 | 7181 | 2160 | 13 | 7 | 0 | 138 |
| | Ag(II) Ion Content (mg/L) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 831 | 0 |
| | pH | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Step 3 Post-treatment Solution | Hydrochloric Acid (g/L) | 200 | 500 | 10 | 50 | 100 | 20 | 0 | 0 | 0 | 50 | 0 | 0 | 200 | 10 | 50 | 100 | — |
| | Sulfuric Acid (g/L) | 0 | 0 | 0 | 0 | 0 | 0 | 100 | 200 | 200 | 0 | 100 | 200 | 0 | 0 | 0 | 0 | — |
| Step 4 Catalyst-adding Solution | Palladium Chloride (mg/L) | 1000 | 500 | 200 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 1000 | 200 | 1 | 0 | 0 |
| | Palladium Sulfate (mg/L) | 0 | 0 | 0 | 0 | 1200 | 600 | 0.2 | 30 | 30 | 0 | 0.1 | 30 | 0 | 0 | 0 | 1200 | 600 |
| | Stannous Chloride (mg/L) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4500 | 0 | 0 | 0 | 0 | 0 |
| Step 5 Electroless Plating Solution | Nickel Sulfate Hexahydrate (g/L) | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 0 | 0 | 40 | 40 | 0 | 40 | 40 | 40 | 40 | 40 |
| | Sodium Acetate (g/L) | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 0 | 0 | 10 | 10 | 0 | 10 | 10 | 10 | 10 | 10 |
| | Sodium Citrate (g/L) | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 0 | 0 | 10 | 10 | 0 | 10 | 10 | 10 | 10 | 10 |
| | Copper Sulphate Pentahydrate (g/L) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 15 | 15 | 0 | 0 | 15 | 0 | 0 | 0 | 0 | 0 |
| | Sodium Hydroxide (g/L) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 10 | 10 | 0 | 0 | 10 | 0 | 0 | 0 | 0 | 0 |
| | EDTA (g/L) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 20 | 20 | 0 | 0 | 20 | 0 | 0 | 0 | 0 | 0 |
| | Dimethylamine Borane (g/L) | 0 | 3 | 4 | 4 | 4 | 3 | 3 | 0 | 0 | 4 | 3 | 0 | 0 | 4 | 3 | 4 | 3 |
| | Formaldehyde (g/L) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 | 5 | 0 | 0 | 5 | 0 | 0 | 0 | 0 | 0 |
| | Sodium Hypophosphite (g/L) | 20 | 0 | 0 | 10 | 10 | 20 | 5 | 0 | 0 | 0 | 5 | 0 | 20 | 0 | 0 | 10 | 20 |
| | pH | 9.0 | 9.0 | 9.0 | 9.0 | 9.0 | 9.0 | 9.0 | 12.5 | 12.5 | 9.0 | 9.0 | 12.5 | 9.0 | 9.0 | 9.0 | 9.0 | 9.0 |
| Deposit Percentage (%) | ABS | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 50 | 25 | 60 | 75 | 80 |
| | PC/ABS | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 45 | 100 | 2 | 15 | 30 | 55 | 30 |
| Peel Strength (N/cm) | ABS | 12.7 | 12.8 | 12.9 | 13.3 | 12.5 | 12.9 | 10.2 | 10.7 | 10.2 | 11.4 | 8.9 | 9.4 | 4.8 | Not Measurable | 9.8 | 2.1 | 6.8 |
| | PC/ABS | 13.9 | 13.6 | 14.8 | 16.2 | 15.5 | 16.4 | 12.6 | 11.4 | 10.1 | 11.5 | 2.1 | 3.3 | Not Measurable | Not Measurable | Not Measurable | 1.5 | Not Measurable |

**[0125]** In Comparative Example 4, as shown in Table 1, the pre-treatment composition was prepared according to the following method in order to dissolve Ag(II). Specifically, after additives other than an Mn salt were dissolved in pure water, anodic electrolysis was performed at 1 Ah/L by using Pt electrodes, thereby forming Ag(II). Subsequently, an Mn salt was added in a predetermined concentration.

## Claims

1. An electroless plating method for a resin material, comprising

    (1) step 1: bringing a surface to be treated of the resin material into contact with a surface conditioner,
    (2) step 2: after step 1, bringing the surface to be treated of the resin material into contact with a pre-treatment composition,
    (3) step 3: after step 2, bringing the surface to be treated of the resin material into contact with a post-treatment solution containing an inorganic acid,
    (4) step 4: after step 3, bringing the surface to be treated of the resin material into contact with a catalyst-adding solution, and
    (5) step 5: after step 4, bringing the surface to be treated of the resin material into contact with an electroless plating solution,

    wherein

    the surface conditioner contains an ether-bond-containing solvent, and
    the pre-treatment composition contains 10 mg/L or more of manganese ions and 10 mg/L or more of monovalent silver ions.

2. The electroless plating method according to claim 1, wherein manganese of the manganese ions has a valence of 3 or more.

3. The electroless plating method according to claim 1 or 2, wherein the inorganic acid is at least one member selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, hydrofluoric acid, and boric acid.

4. The electroless plating method according to any one of claims 1 to 3, wherein the catalyst-adding solution contains 0.1 mg/L or more of a palladium compound and does not contain a tin compound.

5. The electroless plating method according to any one of claims 1 to 4, wherein the resin material is an alloy resin of a styrene-based resin and a polycarbonate (PC) resin.

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**Application Number**
EP 22 18 8523

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