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DESCRIPTION



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Palladium Remover and Removal of Palladium

5 Technical Field

The present invention relates to a palladium remover and a method of removing palladium by the palladium remover, more specifically, to a remover for removing palladium remaining on the surface of a board being treated without damaging the board and a method of removing palladium.

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Background Art

An additive method has been employed as one of the methods for forming circuit patterns. In this method, palladium is deposited on the entire surface of an insulating substrate, and then a copper plating layer is formed on the palladium layer by an electroless plating method. The area of the copper plating layer to form circuit patterns is covered with an etching-resistant resist and the non-covered area of the copper plating layer is etched away. Thereafter, by stripping the residual etching-resistant resist, the circuit patterns are formed.

20 In this conventional method, the surface of the insulating substrate comes out again after the formation of the circuit patterns with the palladium remained thereon. Palladium acts as a plating catalyst in the electroless plating and is effective for easily forming a conductive layer thereon. However, since palladium is hardly soluble to a usual etching solution, it remains not removed after the etching of the copper plating layer. The remaining palladium reduces the insulation of the circuit patterns.

25 The circuit pattern is sometimes surface-treated by electroless nickel plating, electroless gold plating, etc. on its entire surface or its pad portion for connecting another element. Since the palladium remaining on the surface of the insulating surface acts as a plating catalyst, nickel or gold is deposited on

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undesired area of the circuit board, thereby reducing the insulation of the circuit patterns. Therefore, it is quite important to remove the remaining palladium from a circuit board for producing a high quality circuit board. In the conventional additive method, after stripping the etching-resistant resist, the undesirable palladium remaining on the substrate surface has been removed by the following methods.

(1) Method of dissolving away palladium into an iodine/ammonium iodide solution by immersing the board in the solution.

(2) Method of dissolving away palladium into a potassium permanganate solution by immersing the board in the solution.

(3) Method of removing palladium from the substrate surface by a vacuum evacuation apparatus employed in a reactive ion etching (RIE) system, etc.

However, these conventional methods for removing palladium involve the following problems.

(1) In the method of immersing in the iodine/ammonium iodide solution, not only palladium but also copper dissolves into the solution, thereby making the wirings thinner or causing wire break.

(2) In the method of immersing into the potassium permanganate solution, the surface of resin substrate is oxidized to form a finely roughened surface. The oxidation of the resin proceeds faster than the dissolution of palladium.

Therefore, the palladium remover fails to contact palladium remaining in the recess of the oxidized resin surface, thereby leaving palladium partially unremoved.

(3) The method of using the vacuum evacuation apparatus is expensive as compared with the above wet methods. In addition, this method is likely to be limited in the treatment capacity, i.e., the number of boards being treated in one operation. This increases production costs of wiring boards.

Recently, Japanese Patent Application Laid-Open Nos. 3-254179 and 4-179191 propose methods of removing palladium comprising immersing a board in a potassium permanganate solution, optionally ultrasonic-washing the board,

and immersing the board in a solution containing an aromatic nitro compound, an amine compound, an aminocarboxylic acid, a carboxylic acid, sodium hydroxide and hydroxyammonium sulfate. The proposed remover removes the oxidized resin layer on the substrate simultaneously with palladium.

- 5 Therefore, the potassium permanganate solution not only roughens the substrate surface but also corrodes the interface between the copper circuit pattern and the substrate.

Disclosure of Invention

- 10 An object of the present invention is to solve the above problems and provide a palladium remover for removing palladium remaining on a board being treated without damaging the board and a method of removing palladium using the palladium remover. Specifically, the object of the present invention is to provide a palladium remover which causes no corrosion on a wiring
- 15 material and an insulating substrate and easily removes palladium remaining on the surface of an insulating substrate after the formation of circuit patterns in the manufacture of circuit boards, and to provide a method of removing palladium using the palladium remover.

- As a result of intensive study in view of achieving the above object, the
- 20 inventors have found that palladium remaining on an insulating substrate after circuit pattern formation by an additive method is easily removed in short period by a liquid composition comprising (a) a nitrate, (b) a water-solubilizer for making palladium oxide water-soluble, (c) water, and optionally (d) a wetting agent and/or a chelating agent, thereby enhancing the insulation of the
- 25 circuit patterns to provide highly reliable printed circuit boards. The present invention has been accomplished on the basis of this finding.

- Thus, in a first aspect of the present invention, there is provided a palladium remover comprising (a) a nitrate, (b) a water-solubilizer for making palladium oxide water-soluble, and (c) water. The palladium remover may
- 30 optionally contain (d) a wetting agent and/or (e) a chelating agent.

In a second aspect of the present invention, there is provided a method for removing palladium which comprises the steps of forming a palladium layer on a surface of an insulating substrate; forming a copper plating layer on the palladium layer; etching the copper plating layer after applying a resist to a surface of the copper plating layer; stripping a residual resist to form a circuit pattern; and removing palladium remaining on the insulating substrate by the palladium remover.

Brief Description of Drawings

Figs. 1a to 1d are schematic illustrations showing the steps up to the production of a circuit board to be treated with a palladium remover of the present invention in the production of printed wiring board.

Best Mode for Carrying Out the Invention

The nitrate (a) may include ammonium nitrate, lithium nitrate, zinc nitrate, manganese nitrate, nickel nitrate, cobalt nitrate, sodium nitrate, and potassium nitrate with ammonium nitrate being particularly preferable. The nitrate has an oxidizing action on palladium. The concentration of the nitrate in the palladium remover is 0.001 to 40% by weight, preferably 0.005 to 30% by weight.

The water-solubilizer (b) for making palladium oxide water-soluble may be an inorganic acid or its salt, preferably hydrochloric acid, nitric acid, sulfuric acid, hydrochloride such as ammonium chloride and aluminum chloride, and sulfate such as ammonium sulfate and aluminum sulfate. The concentration of the water-solubilizer in the palladium remover is 0.01 to 50% by weight, preferably 0.05 to 30% by weight.

Another substance having an oxidizing action on palladium and/or another substance having a water-solubilizing action on palladium oxide may be combinedly used to enhance the oxidation ability and/or the water-solubilization ability of the palladium remover in an amount not adversely

affecting the effect of the present invention.

The palladium remover may further contain the wetting agent (d) in addition to the components (a) to (c). The wetting agent (c) is a surfactant, an alcohol or an ether. The surfactant may be cationic, nonionic or anionic.

5 Examples of the alcohol may be ethyl alcohol, isopropyl alcohol, butanol, ethylene glycol, diethylene glycol, propylene glycol, and dipropylene glycol. Examples of the ether include ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, propylene glycol
10 monomethyl ether, propylene glycol monoethyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol monobutyl ether, diethylene glycol dimethyl ether, dipropylene glycol dimethyl ether, polyoxyethylene methyl phenyl ether, polyoxyethylene ethyl phenyl ether, polyoxyethylene octyl phenyl
15 ether, and polyoxyethylene nonyl phenyl ether.

The above wetting agents may be used singly or in combination of two or more. The concentration of the wetting agent in the palladium remover is 0.001 to 10% by weight, preferably 0.005 to 5% by weight, and more preferably 0.005 to 1% by weight.

20 In addition to the components (a) to (c) or the components (a) to (d), the palladium remover may further contain a chelating agent (e). The chelating agent is a compound capable of forming a complex with palladium, and may include dimethylglyoxime, thiourea, thioxine (8-mercaptoquinoline), dithizone, 2-nitroso-1-naphthol, and p-nitrosodimethylaniline with dimethylglyoxime and
25 thiourea being preferable.

The chelating agent (e) acts as a water-solubilizer for making palladium oxide water-soluble, and also has an action of forming a complex with palladium remaining in a small amount in the recess of the roughened surface of the insulating substrate. With such formation of the complex, palladium is
30 deactivated against the electroless nickel plating and the electroless gold

plating after the formation of circuit patterns, thereby prevent nickel and gold from depositing on undesired area of the insulating substrate to ensure circuit patterns well insulated.

5 The concentration of the chelating agent in the palladium remover is 0.01 to 5% by weight, preferably 0.01 to 2% by weight, and more preferably 0.05 to 2% by weight.

10 The palladium remover of the present invention is an aqueous liquid comprising the nitrate, the water-solubilizer, optional wetting agent and/or chelating agent, and balance of water. Although the aqueous liquid may be a dispersion or a suspension, usually an aqueous solution.

The palladium removal by the method of the present invention is carried out by immersing a board to be treated in the palladium remover at room temperature to 80 °C. The pH of the palladium remover is 0 to 5, and controlled by changing the addition amount of the inorganic acid as the component (b). The palladium remover is used in an amount enough to effectively remove palladium from the board being treated, and one skilled in the art can easily determine the amount with no undue experiment. By the palladium-removing method of the present invention, a substantially complete removal of palladium remaining on the board after the formation of circuit patterns can be achieved.

The present invention will be described in more detail by reference to the following examples and comparative examples. However, it should be noted that the following examples are only illustrative and the scope of the present invention is not restricted thereto.

25 Fig. 1 is a schematic illustration showing the steps up to the circuit formation in the production of circuit boards. As shown in Fig. 1a, a palladium catalyst layer 2 is formed on an insulating substrate 1. Palladium is usually adsorbed onto the insulating substrate to form a very thin layer, and acts as a catalyst for the electroless plating. On the palladium catalyst layer 2 on the insulating substrate, a conductive layer 3 made of a copper plating layer is

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formed by electroless plating as shown in Fig. 1b. The conductive layer may be formed on the electroless plating surface by electroplating.

Then, as shown in Fig. 1c, a portion of the conductive layer 3 which is to constitute the circuit is covered with a photoresist layer 4, followed by

5 dissolving away the non-covered copper plating layer 3 with an etching solution. The photoresist layer is formed, for example, by a dry photofilm, a photoresist ink, or a screen printing resist. Examples of the etching solution include sulfuric acid-hydrogen peroxide mixed solution, copper(II) chloride solution, and iron(III) chloride solution.

10 As a result of the etching, conductive circuits are formed on the surface of the insulating substrate 1 as shown in Fig. 1d. Even after the etching of the non-masked area of the copper plating layer, palladium 2a remains unremoved on the insulating substrate.

EXAMPLES 1 to 7

15 Each circuit board having palladium remaining thereon as prepared in the manner described above was immersed in respective palladium removers listed in Table 1 under respective conditions, rinsed with pure water, and dried. Then, the insulation resistance between the circuit portions with 20- μ m interval was measured. The amount of the remaining palladium on the
20 insulating substrate was measured by X-ray fluorescence spectroscopy and X-ray microanalyzer. The circuit pattern was subjected to electroless plating with nickel, and the occurrence of nickel deposition on the insulating substrate was observed. Further, the corrosion of the copper circuit pattern was observed. The results of measurements and observations were evaluated
25 according to the following criteria and are shown in Table 1.

1. Insulation

A: several M Ω before treatment and infinite after treatment.

C: several M Ω before treatment and several M Ω after treatment.

2. Palladium removal

30 A: completely removed.

B: partially remained.

C: substantial part remained.

3. Nickel deposition

A⁺: no deposition

5 A: substantially no deposition.

B: slight deposition.

C: considerable deposition.

4. Copper corrosion

A: no corrosion

10 B: partial corrosion

C: corrosion on entire surface.

Table 1

Composition of Palladium Remover							
Nitrate		Water-solubilizer		Wetting Agent		Water	
Kind	wt %	Kind	wt %	Kind	wt %	Kind	wt %
Examples							
1	ammonium nitrate	2	hydrochloric acid	5	—	—	balance
2	ammonium nitrate	5	hydrochloric acid	5	—	—	balance
3	ammonium nitrate	0.5	hydrochloric acid	5	—	—	balance
4	ammonium nitrate	2	hydrochloric acid	1	a*	3	balance
5	ammonium nitrate	2	hydrochloric acid	1	b*	0.1	balance
6	ammonium nitrate	2	sulfuric acid	3	—	—	balance
7	ammonium nitrate	2	nitric acid	5	—	—	balance

a*: Isopropyl alcohol

b*: Polyoxyethylene nonyl phenyl ether

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Table 1 (contd.)

Removing Conditions			Results of Evaluation			
Temperature (°C)	Time (min)	Insulation	Pd Removal	Ni Deposition	Cu Corrosion	
Examples						
1	60	5	A	A	A	A

2	60	5	A	A	A	A
3	70	5	A	A	A	A
4	50	3	A	A	A	A
5	50	3	A	A	A	A
6	60	5	A	A	A	A
7	60	5	A	A	A	A

COMPARATIVE EXAMPLES 1 to 8

The procedure of Examples 1 to 7 was repeated using a palladium remover having each composition listed in Table 2. The results are also shown in Table 5 2.

Table 2

Composition of Palladium Remover							
Nitrate			Water-solubilizer		Wetting Agent		Water
Kind		wt %	Kind	wt %	Kind	wt %	wt %
Comparative Examples							
1	ammonium nitrate	5	—	—	—	—	balance
2	—	—	hydrochloric acid	5	—	—	balance
3	—	—	sulfuric acid	3	—	—	balance
4	—	—	ammonium chloride	5	—	—	balance
5	ammonium nitrate	5	—	—	a*	3	balance
6	ammonium nitrate	5	—	—	b*	0.1	balance
7	—	—	hydrochloric acid	5	a*	3	balance
8	—	—	ammonium chloride	5	a*	3	balance

a*: Isopropyl alcohol

b*: Polyoxyethylene nonyl phenyl ether

Table 2 (contd.)

Removing Conditions			Results of Evaluation			
Temperature (°C)	Time (min)	Insulation	Pd Removal	Ni Deposition	Cu Corrosion	
Comparative Examples						
1	60	5	C	C	C	A

2	60	5	B	B	C	A
3	60	5	C	C	C	A
4	60	5	C	C	C	A
5	60	5	C	C	C	A
6	60	5	C	C	C	A
7	60	5	B	B	C	A
8	60	5	C	C	C	A

EXAMPLES 8 to 9

The procedure of Examples 1 to 7 was repeated except for using the palladium removers containing the chelating agent. The results are shown in Table 3.

Table 3

Composition of Palladium Remover							
Nitrate			Water-solubilizer		Wetting Agent		Water
	Kind	wt %	Kind	wt %	Kind	wt %	wt %
Examples							
8	ammonium nitrate	2	hydrochloric acid	1	c*	0.1	balance
9	ammonium nitrate	2	hydrochloric acid	1	d*	0.1	balance

c*: Dimethylglyoxime

d*: Thiourea

Table 3 (contd.)

Removing Conditions			Results of Evaluation			
Temperature (°C)	Time (min)	Insulation	Pd Removal	Ni Deposition	Cu Corrosion	
Examples						
8	50	3	A	A	A ⁺	A
9	50	3	A	A	A ⁺	A

Industrial Applicability

Palladium remaining on a circuit board is removed by immersing the board in the palladium remover of the present invention. The palladium remover of the invention is particularly suitable for removing palladium

remaining on the insulating substrate without corroding the copper circuit and roughening the surface of the insulating substrate, thereby enhancing the insulation of the circuit pattern.

- 5 In addition, when the circuit pattern is treated by electroless nickel plating or electroless gold plating, the lowering of the insulation caused by the deposition of nickel or gold on the non-circuit area of the insulating substrate is effectively prevented.

CLAIMS

1. A palladium remover comprising (a) a nitrate, (b) a water-solubilizer for making palladium oxide water-soluble, and (c) water.
- 5 2. The palladium remover according to claim 1, comprising 0.001 to 40% by weight of the nitrate, 0.01 to 50% by weight of the water-solubilizer, and a balance of water.
3. The palladium remover according to claim 1 or 2, wherein the nitrate is at least one compound selected from the group consisting of ammonium nitrate,
10 lithium nitrate, zinc nitrate, manganese nitrate, nickel nitrate, cobalt nitrate, sodium nitrate, and potassium nitrate.
4. The palladium remover according to any one of claims 1 to 3, wherein the water-solubilizer is at least one compound selected from the group consisting of hydrochloric acid, nitric acid, sulfuric acid, ammonium chloride, aluminum
15 chloride, ammonium sulfate and aluminum sulfate.
5. The palladium remover according to any one of claims 1 to 4, further comprising (d) a wetting agent.
6. The palladium remover according to claim 5, containing 0.001 to 10% by weight of the wetting agent.
- 20 7. The palladium remover according to claim 5 or 6, wherein the wetting agent is a surfactant, an alcohol or an ether.
8. The palladium remover according to claim 7, wherein the surfactant is cationic, nonionic or anionic.
9. The palladium remover according to claim 7, wherein the alcohol is at
25 least one compound selected from the group consisting of ethyl alcohol, isopropyl alcohol, butanol, ethylene glycol, diethylene glycol, propylene glycol, and dipropylene glycol.
10. The palladium remover according to claim 7, wherein the ether is at least one compound selected from the group consisting of ethylene glycol monoethyl
30 ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether,

diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol monobutyl ether, diethylene glycol
5 dimethyl ether, dipropylene glycol dimethyl ether, polyoxyethylene methyl phenyl ether, polyoxyethylene ethyl phenyl ether, polyoxyethylene octyl phenyl ether, and polyoxyethylene nonyl phenyl ether.

11. The palladium remover according to any one of claims 1 to 10, further comprising (e) a chelating agent.

10 12. The palladium remover according to claim 11, containing 0.01 to 5% by weight of the chelating agent.

13. The palladium remover according to claim 11 or 12, wherein the chelating agent is at least one compound selected from the group consisting of dimethylglyoxime, thiourea, thioxine (8-mercaptoquinoline), dithizone, 2-
15 nitroso-1-naphthol, and p-nitrosodimethylaniline.

14. The palladium remover according to any one of claims 1 to 13, for use in the production of circuit board by additive method where a circuit pattern is formed by a copper plating layer deposited on the surface of an insulating substrate.

20 15. A method of removing palladium comprising the steps of:
forming a palladium layer on a surface of an insulating substrate;
forming a copper plating layer on the palladium layer;
etching the copper plating layer after applying a resist to a surface of the copper plating layer;
25 stripping a residual resist to form a circuit pattern; and
removing palladium remaining on the insulating substrate by the palladium remover as defined in any one of claims 1 to 13.