

Description

This invention relates to a process for treating surfaces of copper conductors of wiring boards for inner layers which are bonded via prepregs in the production of multilayer printed wiring boards.

6 Multilayer printed wiring boards are usually produced by the following processes:

(1) One process comprises forming printed copper conductors by etching the copper foils of copper clad laminates to give printed wiring boards for inner layers, treating the surfaces of the copper conductors with a chemical solution of ammonium persulfate, cupric chloride or copper acetate to roughen them, laminating and adhering copper clad laminates for outer layers via prepregs (products of impregnating base materials such as paper and glass fabrics with thermosetting resins, followed by drying them) on one or more thus treated inner layer printed wiring boards, drilling or punching through holes at predetermined portions including the copper conductors of inner layers, immersing in a sensitizing solution, forming electroless copper plated layers on the walls of the through-holes, and etching the copper foils of the outer layers in accordance with the inner copper conductors pattern to form outer layer copper conductors.

(2) Another process comprises subjecting one or more copper clad laminates, which have roughened copper foils on both sides to improve adhesiveness and the like (both-side roughened copper foils), to the same treatment as in the process (1) to give printed wiring boards for inner layers, omitting the surface roughening step, laminating and adhering copper clad laminates for outer layers via prepregs on one or more thus treated inner layer printed circuit boards, followed by the same procedures as described in process (1) to give a multilayer printed wiring board.

(3) A further process comprises forming printed wiring boards for the inner layers in the same manner as described in the process (1), roughening the copper conductor surfaces in the same manner as described in the process (1), treating with a sodium chlorite-sodium hydroxide-trisodium phosphate treating solution, forming copper oxide films (1-3 μm) on the roughened copper conductor surfaces, laminating and adhering copper clad laminates as outer layers via prepregs on one or more thus treated inner layer printed circuit boards, followed by the same procedures as described in the process (1) to give a multilayer printed wiring board.

These process have following disadvantages:

30 Multilayer printed wiring boards produced by process (1) have insufficient adhesive strength between the inner layer copper conductors and the resin layers obtained by curing the prepregs. Further, when mounting various electronic devices on the thus-produced multilayer printed wiring board with solder, peeling occurs between the inner layer copper conductors and the resin layer obtained by curing the prepregs; sometimes blisters derived from the peeling can be identified by the naked eye from outside.

35 In the process (2), since a both-side roughened copper foil is used, the roughened surface sometimes becomes scratched during the steps prior to formation of the printed wiring on the copper clad laminates. In such a case, the scratched portion has lower adhesive strength. Further, since the roughened surface of a copper foil is used, the pattern definition of the printing etching resist, or the pattern definition of the etching resist used in a UV photographic printing method for forming printed wiring patterns, is poor.

40 In the process (3), the copper oxide film is dissolved by the sensitizing solution used when providing a plating catalyst on through-hole surfaces for forming electroless copper plated films thereon (the sensitizing solution being an acidic solution of pH 4 or less) or by an acidic solution used when removing smears adhered to cut surfaces of inner layer copper conductors after drilling through-holes and the acidic solution permeates between inner layer copper conductor surfaces and resin layers to bring about the pink-ring phenomenon and lower both the adhesiveness between the inner layer copper conductor surface and the resin layer obtained by curing the prepreg and the insulation resistance between conductors.

USA-3793038 describes electroless plating onto catalysed surfaces of plastic articles in which various organo-nitrogen compounds are used to stabilise the plating solution.

50 It is an object of this invention to provide a process for treating surfaces of copper to improve adhesion to a resin material such as a prepreg used in the production of multilayer printed wiring boards.

This invention provides a process comprising treating a copper conductor surface with a liquid composition comprising

- (I) copper ions, a complexing agent for copper ions, a reduction agent for copper ions, a pH adjusting agent, water and
- 55 (II) at least one nitrogen-containing organic compound selected from 2,4,6-tris(2-pyridyl)-s-triazine; α , α' , α'' -tripyridyl; 1,10-phenanthroline; 4,7-diphenyl-1,10-phenanthroline; 4,7-dimethyl-1,10-phenanthroline; 4,7-diphenyl-1,10-phenanthroline disulphonic acid disodium salt; 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine; α , α' -dipyridyl; Phthalocyanine Green; 2,4-dimethyl-imidazoline, 8-azaguanine; xanthopterin; 5-aminoin-

dazole; 2-aminopyrimidine hydrochloride; 2-amino-pyrimidine hydrobromide; benzoguanamine; acriflavine hydrochloride; 5-amino-1H-tetrazole; 6-amino-2-phenyl-4-guainolinol; 2-amino-6,8-dihydroxypurine; 2-aminopyrimidine; 6-hydroxy-2,4,5-triaminopyrimidine sulphate; 2,4-diamino-6-hydroxypyrimidine; 2-amino-4-hydroxy-6-methylpyrimidine; 4,6-dihydroxypyrimidine; nitroguanidine; 1-hydroxy 1H-benzotriazole monohydrate; 2-hydroxybenzimidazole and 2-amino-3-hydroxypyridine forming an electroless copper deposition layer having an average light absorption rate of 0.5 or more using a light of 300 to 800 nm and converted to values so as to meet the wavelength intensity distribution of sunlight and bonding a resin to the electroless copper deposition layer.

The attached drawing is a cross-sectional view showing the arrangement of materials for producing a multi-layer printed wiring board.

The liquid composition (hereafter "treating solution A") comprises (I) copper ions, a complexing agent for copper ions, a reducing agent for copper ions, a pH adjusting agent, water, and (II) a nitrogen-containing organic compound.

As the copper ions, there can be used those obtained from a copper ion source such as copper sulphate, copper nitrate and cupric chloride, and other conventional copper salts.

As the complexing agent for copper ions, there can be used compounds which form complexes with the above-mentioned copper ions and make the complexes soluble in an aqueous alkaline solution. Examples of the complexing agents are ethylenediaminetetraacetic acid (EDTA) or sodium salts (mono-, di-, tri- or tetrasodium salts) thereof;

N,N,N',N'-tetrakis(2-hydroxy-propyl)-ethylenediamine; nitrilotriacetic acid and its alkali salts; gluconic acid; gluconates; triethanolamine and tartaric acid.

As the reducing agent for copper ions, there can be used for instance formaldehyde and formaldehyde precursors or derivatives, such as paraformaldehyde and hypophosphites.

As the pH adjusting agent for adjusting the pH of the treating solution A, there can be used for instance sodium hydroxide or potassium hydroxide.

As the water, the use of deionized water is preferable.

The preferred composition of component (I) is as follows:

copper ions	0.004 - 0.1 mole/liter
complexing agent	0.004 - 0.2 mole/liter
reducing agent	0.01 - 0.25 mole/liter
pH	11.0 - 13.4

A particular example of the component (I) is as follows:

CuSO₄·5H₂O	2 - 20 g/liter
ethylenediaminetetraacetic acid:	
[CH₂N(CH₂COOH)₂]₂	1 - 5 moles/mole of CuSO₄
37% formalin:	2 - 20 ml/liter
pH:	11.0 - 13.5

Component (II) is usually used in an amount of 0.1 mg/liter or more. Since the nitrogen-containing organic compounds mentioned above are relatively expensive, the addition of too large an amount is not preferable from the viewpoint of production cost. It is preferable to use in the range of 1 to 500 mg/liter. These compounds of the component (II) are available commercially from for instance Dojindo-Laboratories Co., Ltd., Tokyo Kasei Kogyo Co., Ltd and Aldrich Chemical Co. in U.S.A.

Treating solution A is fundamentally an electroless copper deposition bath used for forming conductors on insulating substrates in the production of printed wiring boards. But the electroless copper deposition bath conventionally used is so composed as to form an electroless copper deposition having a metallic copper color and metallic copper gloss on the insulating substrates by adding various additives to the component (I). In contrast, in the present invention, the component (II) is added to the component (I) so as to form an electroless copper deposition having a color and gloss other than those of metallic copper obtained by the conventionally used electroless copper deposition bath on a surface of metal such as copper.

By treatment with the treating solution A, there can be formed an electroless copper deposition layer having minute particles, needles, cylinders, or a mixture thereof in the layer as deposited surface morphology. Such an electroless copper deposition layer has a dark color such as dark brown, grayish brown, bluish violet, bluish black or brownish black with no gloss. Such a color has an average light absorption rate of 0.5 or more, preferably 0.7 or more, using a light of 300 to 800 nm and converted to values so as to meet the wavelength intensity distribution of sunlight.

The temperature of the treating solution A depends mainly on the pH and the concentration of reducing agent in treating solution A. When the pH or the reducing agent concentration is high, treatment is possible even at low temperatures. Therefore, it is possible to select the temperature from room temperature to about 90°C depending on the composition of the treating solution A.

The treatment time is related to the deposition rate of the treating solution A. Since a shorter treating time is preferable, the immersion time in the treating solution A is usually 1 to 60 minutes.

The thickness of the plated film is preferably 1 to 5 μm. But even if the thickness is over 5 μm, this is no obstacle to improvement in adhesiveness.

After the treatment of the metal surface with the treating solution A, the treatment with at least one of ammonia water, an aqueous solution containing a reducing agent and an acid solution (hereinafter referred to as "treating solution B") can give more desirable results.

The treatment with ammonia water can be carried out by selecting the concentration, the treating temperature and the treating time properly so as to remove impurities such as cuprous oxide coprecipitated on the metallic copper layer obtained by the treatment with the treating solution A.

The aqueous solution containing a reducing agent can be prepared by using formaldehyde, paraformaldehyde, hypophosphorous acid or a salt thereof, as a reducing agent. In the case of using formaldehyde or paraformaldehyde, it is preferable to make the aqueous solution alkaline in the pH range of 9.0 to 13.5 in order to provide reducing properties. It is possible to add a complexing agent for copper ions to the reducing aqueous solution. It is also possible to use an electroless copper deposition solution containing a copper salt, hydroxyl ions, a complexing agent for copper ions, and formaldehyde but avoid an electroless copper deposition reaction by having too low a concentration of copper salts. Even in these cases, the concentration of for instance the reducing agent, the temperature of the solution B and the treatment time can be selected properly so as to achieve the maximum adhesive strength between the treated surface and the resin so long as the glossless and dark colored surface obtained by the treatment with treating solution A is retained.

In the case of acid solution, there can be used an aqueous solution of hydrochloric acid, sulfuric acid or ammonium persulfate. The concentration, the temperature and the treatment time of the acid solution can be selected properly so as to achieve the maximum adhesive strength between the treated surface and the resin so long as the glossless and dark colored surface obtained by the treatment with treating solution A is retained.

When treatment with the treating solution B is conducted after treatment with a sodium chlorite-sodium hydroxide-trisodium phosphate solution employed in the prior art process (3) mentioned above, the adhesive strength between the treated surface and the resin is remarkably lowered compared with the prior art process.

In contrast, according to this invention, since treatment with the treating solution B is conducted after the treatment with treating solution A, the adhesive strength between the treated surface and the resin can be improved compared with the case when the only treatment is with treating solution A.

The treatment with treating solution A or B can be conducted by conventional processes such as dipping or spraying.

The copper conductors to be treated by this invention can be conductors obtained by either etching the copper foil of copper clad laminates, electroless copper plating of a combination of electroless and electroplating of copper.

Before applying the surface treatment of copper according to this invention, the surface of the metal, such as wiring patterns on inner layer laminates, can be pre-treated with an aqueous solution of at least one compound selected from hydrochloric acid, sulphuric acid, nitric acid, phosphoric acid, acetic acid, copper compounds such as cupric chloride and copper sulphate, iron compounds such as ferric chloride and ferric sulfate, alkali metal chlorides or ammonium persulfate, to "roughen" the surface. It is also possible to employ mechanical methods such as liquid honing and abrasion, in place of a chemical "roughening" method.

This invention was explained in relation to the treatment of copper conductors to increase the adhesion of wiring patterns on inner layer printed wiring boards, but the treating solution A or A and B used in this invention can also be used for surface treatment of the copper of copper clad laminates to increase the

adhesive strength between the copper and a resist which is formed on the copper or surface. It can also be used as a surface treatment of copper conductors to increase the adhesion between the copper conductor surface and a solder resist. That is, when treatment according to this invention is conducted after the formation of copper conductors by an etching method or an additive method, and an insulating resin, e.g. a resist ink or an adhesive is coated or adhered by a screen printing method, a curtain coating method or a hot roll laminating method followed by formation of copper conductors, the adhesive strength between the copper conductor surface and the above-mentioned material can be improved remarkably. Thus, a multilayer printed wiring board can be produced without using a pressing step, when conductors are formed on the outer layers of above-mentioned material according to a conventional method.

This invention can also be applied to the treatment of the surface of a copper foil to be contacted with a prepreg in the production of copper clad laminates by bonding a laminate of the copper foil and the prepreg, and the treatment of the surface of a copper foil to be contacted with a flexible film in the production of substrates for flexible wiring boards by bonding the copper foil and the flexible film.

As mentioned above, according to this invention, the adhesive strength between a resin material, such as a prepreg, and copper is improved, the line definition of the inner layer conductors in multilayer printed wiring boards is excellent, and thus there can be obtained printed wiring boards for inner layers having excellent adhesive strength and shelf life.

This invention is illustrated by way of the following Examples and Comparative Examples, in which all percents are by weight unless otherwise specified.

Example 1

A copper clad laminate wherein an epoxy resin was used which had previously been subjected to a roughening treatment with ammonium persulphate aqueous solution. Then, it was immersed in a treating solution obtained by adding 3 mg/liter of 4,7-dimethyl-1,10-phenanthroline to a fundamental bath composition (A₁) at 70 ± 2° C for 20 minutes.

Fundamental bath composition (A₁)

CuSO₄·5H₂O	10 g/liter
EDTA·2Na	40 g/liter
37% HCHO	5 ml/liter
pH (room temp)	12.0
Deionized water	an amount making the
	total volume 1 liter

The color of the treated copper surface, and the results of a tape test and a test for shelf life are listed in Table 1.

The tape test was carried out to examine the adhesive strength of the treated surface. A pressure-sensitive adhesive tape 10 mm wide and with an adhesive on one side (manufactured by Nitto Electric Industrial Co., Ltd.) was attached to the treated surface and stuck tightly until the tape become transparent. Then, the tape was peeled off gradually and the amount of the adhesive remaining on the treated surface was evaluated. The larger the amount of adhesive remaining, the higher the adhesive strength. The adhesive strength was evaluated as follows: X no adhesive was retained; ▲ the adhesive was retained slightly; ○ the adhesive was retained on about half of the surface; and ⊙ the adhesive was retained on the whole surface.

The shelf life test was conducted to examine the period of usable time for bonding with lamination without lowering the adhesive strength. After being allowed to stand at room temperature at ambient moisture for 7 days, the above-mentioned tape test was conducted on the treated surface and evaluated in the same manner as mentioned above.

Example 2

The process of Example 1 was repeated except using 100 3mg/liter of 1,10-phenanthroline in place of mg/liter of 4,7-dimethyl-1,10-phenanthroline and making the immersion time 30 minutes in place of 10 minutes.

The color of the treated copper surface and the results of the tape test and the shelf life test are listed in Table 1.

Example 3

The process of Example 1 was repeated except using 10 mg/liter of α,α' -dipyridyl in place of 3 mg/liter of 4,7-dimethyl-1,10-phenanthroline.

The color of the treated copper surface and the results of the tape test and the shelf life test are listed in Table 1.

Example 4

The process of Example 1 was repeated except using 20 mg/liter of 2,4,6-tris(2-pyridyl)-s-triazine in place of 3 mg/liter of 4,7-dimethyl-1,10-phenanthroline and making the immersion time 5 minutes in place of 10 minutes.

The color of the treated copper surface and the results of the tape test and the shelf life test are listed in Table 1.

Example 5

The process of Example 1 was repeated except using 10 mg/liter of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine in place of 3 mg/liter of 4,7-dimethyl-1,10-phenanthroline and making the immersion time 30 minutes in place of 10 minutes.

The color of the treated copper surface and the results of the tape test and the shelf life test are listed in Table 1.

Comparative Example 1

A copper clad epoxy resin laminate was subjected to a roughening treatment with aqueous ammonium persulphate solution.

The color of the treated copper surface and the results of the tape test and the shelf life test are listed in Table 1.

TABLE 1

Table 1

Example No.	Color of treated surface	Tape test	Shelf life
Example 1	Bluish violet	⊙	⊙
"	Bluish violet	⊙	⊙
"	Bluish black	⊙	⊙
"	Bluish black	⊙	⊙
"	Dark brown	⊙	⊙
Comparative Example 1	Copper color	x	x

55 Example 6

Inner layer circuits were formed on a copper clad laminate (two-sided board) wherein an epoxy resin was used to give a printed circuit board, which was treated as follows:

The printed circuit board was subjected to degreasing, roughening with aqueous ammonium persulphate solution, rinsing with water, immersion in a treating solution obtained by adding 10 mg/liter of 4,7-dimethyl-1,10-phenanthroline to the fundamental bath composition (A₁) as used in Example 1 at 70 °C for 10 minutes, rinsing with water, and drying at 100 °C for 30 minutes. The resulting printed circuit board was subjected to pressing with heating with prepregs 3 and copper foils 4 as shown in the attached drawing (pressure 60 kg/cm², temperature 170 °C, time 120 minutes) to give a multilayer printed circuit board. In the attached drawing, numeral 1 denotes an inner layer circuit substrate and numeral 2 a circuit copper foil formed on the inner layer circuit substrate.

Properties of the resulting multilayer printed circuit board are shown in Table 2.

Comparative Example 2

Inner layer circuits were formed on a copper clad laminate (two-sided board) wherein an epoxy resin was used to give a printed circuit board, which was treated as follows.

The printed circuit board was subjected to degreasing, roughening with aqueous ammonium persulphate solution, rinsing with water, and drying at 100 °C for 30 minutes. Using the thus treated printed circuit board a multilayer printed circuit board was produced in the same manner as described in Example 6.

Properties of the resulting multilayer printed circuit board are shown in Table 2.

Comparative Example 3

Inner layer circuits were formed on a copper clad laminate (two-sided board) wherein an epoxy resin was used to give a printed circuit board, which was treated as follows.

The printed circuit board was subjected to degreasing, roughening, washing with water, immersion in aqueous solution (sodium hydroxide 0.5%, trisodium phosphate 1% and sodium chlorite 3%) at 70 °C for 1 minute, rinsing with water, and drying at 100 °C for 30 minutes. Using the thus treated printed circuit board, a multilayer printed circuit board was produced in the same manner as described in Example 6.

Properties of the resulting multilayer printed circuit board are shown in Table 2.

Comparative Example 4

Inner layer circuits were formed on a copper clad laminate (two-sided board) having both-side roughened copper foil wherein an epoxy resin was used to give a printed circuit board. Using the printed circuit board, a multi-layer printed circuit board was produced in the same manner as described in Example 6.

Properties of the resulting multilayer printed circuit board are shown in Table 2.

Table 2

Example No.	Adhesive strength (kg/cm)	*1	Line definition of inner layer conductors	*2	Shelf life
Example 6	1.0		Excellent		Adhesiveness did not deteriorate after standing at room temp. and ambient moisture for 7 days.
Comparative Example 2	0.3		Excellent		Adhesiveness was low as an initial value after standing at room temp. and ambient moisture for 7 days.
Comparative Example 3	1.2		Excellent		Adhesiveness deteriorated after standing at room temp. and ambient moisture for 2 days.
Comparative Example 4	1.0		Poor		Adhesiveness did not deteriorate after standing at room temp. and ambient moisture for 7 days.

Note:

*1: Values obtained by peeling an inner layer copper foil according to JIS-C6481.

*2: Excellent = Linearity at line edge was good.

Poor = Line edge lies in a zigzag line.

Examples 7 to 11

Copper clad laminates for inner layers previously provided with inner layer circuits were subjected to a roughening treatment with aqueous ammonium persulphate solution, followed by a treatment with the following treating solution (A₂) for 15 minutes under the following conditions:

CuSO$\cdot$5H₂O	5 g/liter
ETDA.2Na	20 g/liter
37% HCHO	4.0 ml/liter
4,7-Dimethyl-1,10-phenanthroline	5 mg/liter
pH (room temp)	12.3
Deionized water	an amount making the
	total volume 1 liter
Bath temperature	70 $\pm$2°C

Subsequently, the treated inner layer copper clad laminates were treated with a treating solution B and treating conditions as listed in Table 3.

Table 3

Example No.	Treating solution B	Temperature of treating soln. B (°C)	Treating time
7	1% HCl aqueous solution	20 - 25	30 sec
8	5% ammonium persulfate	20 - 25	1 min
9	5% ammonia water	20 - 25	10 min
10	37% HCHO (4 ml/liter) pH = 12.3 Deionized water: an amount making the total volume 1 liter	70 ± 2	30 min
11	37% HCHO (4 ml/liter) pH = 12.0 EDTA-2Na (30 g/liter) CuSO ₄ ·5H ₂ O (0.5 g/liter) Deionized water: an amount making the total volume 1 liter	70 ± 2	30 min

The resulting inner layer copper clad laminates were subjected to pressing with heating with preregs 3 and copper foils 4 as shown in the attached drawing (pressure 60 kg/cm², temperature 170° C, time 120 minutes) to give multilayer printed circuit boards.

5 Properties of the multilayer printed circuit boards were tested and are listed in Table 4.

Adhesive strength: JIS-C 6481 (see footnote of Table 2).

Resistance to HCl aqueous solution: A sample of 130 x 30 mm was cut off and surface copper foils thereon were removed. After drilling 36 holes each with a diameter of 1 mm, the resulting sample was dipped in 18% aqueous HCl solution. The time required for making the HCl penetrate into the inner layer surface was evaluated as follows:

- o: no penetration in all 36 holes,
- Δ: 1 to 5 holes among 36 holes were penetrated and,
- x: 6 or more holes among 36 holes were penetrated.

Resistance to electroless copper deposition bath:

15 A sample of 130 x 30 mm was cut off and surface copper foils thereon were removed. After drilling 36 holes each with a diameter of 1mm, the resulting sample was dipped in the following electroless copper deposition bath. The time required for making the electroless copper deposition bath penetrate into inner layer surfaces was evaluated as follows:

- o: 36 holes were not penetrated,
- 20 Δ: 1 to 5 holes among 36 holes were penetrated, and
- x: 6 or more holes among 36 holes were penetrated.

Electroless copper deposition bath:

CuSO₄ · 5H₂O

10 g/liter

25

EDTA.4Na

30 g/liter

37% HCHO

30

aq. solution

4 ml/liter

pH (room temp.)

12.3

Deionized water

an amount making

35

the total volume

1 liter.

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Comparative Example 5

45 A copper clad laminate for inner layers previously provided with inner layer circuits was subjected to a roughening treatment with aqueous ammonium persulphate solution, following by immersion in an aqueous solution containing 0.5% of NaOH, 1% of trisodium phosphate and 3% of sodium chlorite at 70° C for 1 minute. The thus treated copper clad laminate was subjected to pressing with heating in the same manner as described in Examples 7-11 to give a multilayer printed circuit board.

Properties of the multilayer printed circuit board were tested and are listed in Table 4.

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Comparative Example 6

55 A copper clad laminate for inner layers treated with aqueous ammonium persulphate solution and an aqueous solution containing NaOH, trisodium phosphate and sodium chlorite in the same manner as described in Comparative Example 5 was subjected to the same treatment with the treating solution B as described in Example 7. Then, the thus treated copper clad laminate was subjected to pressing with heating in the same manner as described in Examples 7-11 to give a multilayer printed circuit board.

Properties of the multilayer printed circuit board were tested and listed in Table 4.

Reference Example 1

The process of Examples 7-11 was repeated except that the treatment with a treating solution B was omitted. A multilayer printed circuit board was prepared in the same manner as described in Examples 7-11.

Properties of the multilayer printed circuit board were tested and are listed in Table 4.

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Table 4

Example No.	Adhesive strength (kgf/cm)	Resistance to HCl (min)						Resistance to electroless copper deposition bath (min)					
		20	30	40	50	60	90	20	30	40	50	60	90
Example 7	1.04	o	o	o	o	o	o	o	o	o	o	o	o
" 8	1.06	o	o	o	o	o	o	o	o	o	o	o	o
" 9	1.05	o	o	o	o	o	Δ	o	o	o	o	o	o
" 10	1.07	o	o	o	o	o	Δ	o	o	o	o	o	o
" 11	1.06	o	o	o	o	o	Δ	o	o	o	o	o	o
Comparative Example 5	1.06	x	x	x	x	x	x	Δ	x	x	x	x	x
Comparative Example 6	0.32	o	o	o	o	o	o	o	o	o	o	o	o
Reference Example 1	1.00	o	Δ	x	x	x	x	o	Δ	x	x	x	x

As shown in Table 4, Examples 7 - 11 are remarkably improved in adhesive strength, resistance to HCl aqueous solution, and resistance to electroless copper deposition bath compared with Reference Example 1 wherein no treatment with the treating solution B is conducted.

In Comparative Example 6, the resistance to aqueous HCl solution and the resistance to electroless copper deposition bath are good, but peeling occurs at the adhered surface depending on soldering temperature when parts are mounted on the multilayer printed circuit board with solder due to low inner layer peeling strength.

Example 12

Copper clad laminates wherein an epoxy resin was used were subjected to a roughening treatment with aqueous ammonium persulphate solution, followed by immersion in a treating solution obtained by adding 10 mg/liter of benzoguanamine, 8-azaguanine, xanthopterin, 2-aminopyrimidine-hydrochloride, 2-aminopyrimidine, 6-hydroxy-2,4,5-triaminopyrimidine-sulphate or nitroguanidine to a fundamental bath composition (A₃) at 70 ± 2 °C for 5 minutes.

Fundamental bath composition (A₃)

CuSO ₄ ·5H ₂ O	10 g/liter
EDTA·2Na	40 g/liter
pH (room temp. with NaOH)	12.5
37% HCHO	4 ml/liter
Deionized water	an amount for making the total volume 1 liter

The color of treated copper surface was observed and the tape test and the shelf life test were carried out as described in Example 1.

The results are listed in Table 5 together with those of Comparative Example 1.

Table 5

Example No.	Adding compound	Color of treated surface	Tape test	Shelf life
Run No. 1	Benzoguanamine	Brown	⊙	⊙
" 2	8-Azaguanine	Brown	⊙	⊙
" 3	Xanthopterin	Brown	⊙	⊙
" 4	2-Aminopyrimidine·hydrochloride	Brown	⊙	⊙
" 5	2-Aminopyrimidine	Brown	○	○
" 6	6-Hydroxy-2,4,5-triaminopyrimidine·sulphate	Brown	○	○
" 7	Nitroguanidine	Brown	⊙	⊙
Comparative Example 1	-	Copper color	x	x

Example 13

Inner layer circuits were formed on copper clad laminates (two-sided boards) wherein an epoxy resin was used to give printed wiring boards, which were treated as follows:

The printed wiring boards were subjected to degreasing, roughening with aqueous ammonium persulphate solution, rinsing with water, immersion in a treating solution obtained by adding 15 mg/liter of xanthopterin, 2-aminopyrimidine-hydrochloride or nitroguanidine to the fundamental bath composition (A₃) used in Example 12 at 70°C for 5 minutes, rinsing with water, and drying at 100°C for 30 minutes. The resulting printed circuit board was subjected to pressing with heating in the same manner as described in Example 6 to give multilayer printed wiring boards.

Properties of the multilayer printed wiring boards were tested and listed in Table 6.

Adhesive strength: JIS-C6481 (see footnote of Table 2)

**Line definition
of inner layer**

conductors: See footnote of Table 2.

Shelf life: See Example 1.

Resistance to HCl

aqueous solution: See Examples 7 to 11.

Example 14

The process of Example 13 was repeated except that treatment with a treating solution B (1% aqueous HCl solution) at 20-25°C for 30 seconds was inserted after the treatment with the modified fundamental bath composition (A₃).

Properties of the produced multilayer printed wiring boards were tested and are listed in Table 6.

Table 6

Example No.	Adding compound	Adhesive strength (kg/cm)	Line definition of inner layer conductors	Shelf life	Resistance to HCl (min)				
					20	30	60	120	180
Example 13	Xanthopterin	1.3	Excellent	Adhesiveness did not deteriorate after standing at room temp. and ambient moisture for 7 days	o	o	o	o	o
	2-Aminopyrimidine·hydrochloride	1.2	Excellent		o	o	o	o	o
	Nitroguanidine	1.2	Excellent		o	o	o	o	o
Example 14	Xanthopterin	1.5	Excellent	Adhesiveness did not deteriorate after standing at room temp. and ambient moisture for 7 days	o	o	o	o	o
	2-Aminopyrimidine·hydrochloride	1.4	Excellent		o	o	o	o	o
	Nitroguanidine	1.3	Excellent		o	o	o	o	o
Comparative Example 2	-	0.3	Excellent	Adhesiveness was low as an initial value after standing at room temp. and ambient moisture for 7 days.	x	x	x	x	x

- Cont'd -

Table 6 (Cont'd)

Compara- tive Example 3	-	1.2	Excellent	Adhesiveness deteriorated after standing at room temp. and ambient moisture for 2 days.	x	x	x	x	x
Compara- tive Example 4	-	1.0	Poor	Adhesiveness did not deteriorate after standing at room temp. and ambient moisture for 7 days.	o	o	o	o	o



5 Claims

1. A process comprising treating a copper conductor surface with a liquid composition comprising
 (i) copper ions, a complexing agent for copper ions, a reduction agent for copper ions, a pH
 adjusting agent, water and
 10 (ii) at least one nitrogen-containing organic compound selected from 2,4,6-tris(2-pyridyl)-s-triazine; α , α' , α'' -tripyridyl; 1,10-phenanthroline; 4,7-diphenyl-1,10-phenanthroline; 4,7-dimethyl-1,10-phenanthroline; 4,7-diphenyl-1,10-phenanthroline disulphonic acid disodium salt; 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine; α , α' -dipyridyl; Phthalocyanine Green; 2,4-dimethyl-imidazoline, 8-azaguanine; xanthopterin; 5-aminoindazole; 2-aminopyrimidine hydrochloride; 2-amino-pyrimidine hydrobromide; benzoguanamine; acriflavine hydrochloride; 5-amino-1H-tetrazole; 6-amino-2-phenyl-4-quinolinol; 2-amino-6,8-dihydroxypurine; 2-aminopyrimidine; 6-hydroxy-2,4,5-triaminopyrimidine sulphate; 2,4-diamino-6-hydroxypyrimidine; 2-amino-4-hydroxy-6-methylpyrimidine; 4,6-dihydroxypyrimidine; nitroguanidine; 1-hydroxy 1H-benzotriazole monohydrate; 2-hydroxybenzimidazole and 2-amino-3-hydroxypyridine forming an electroless copper deposition layer having an average light absorption
 15 rate of 0.5 or more using a light of 300 to 800 nm and converted to values so as to meet the wavelength intensity distribution of sunlight and bonding a resin to the electroless copper deposition layer.
2. A process according to claim 1, wherein the electroless copper deposition layer has an average
 25 absorption rate of 0.7 or more.
3. A process according to claim 1 or claim 2 wherein the liquid composition comprises from 1 to 500 mg/l of the nitrogen-containing organic compound.
- 30 4. A process according to any one of the preceding claims, which further comprises treating the electroless copper deposition layer with at least one of ammonia water, an aqueous solution containing a reducing agent and an acid solution prior to bonding a resin to the layer.
5. A process according to any one of claims 1 to 4 which further comprises bonding further resin layers to
 35 the surface-treated metal to give a laminate of one or more metal layers and more than one resin layer.
6. A process according to any one of claims 1 to 5 wherein the liquid composition comprises at least one nitrogen-containing organic compound selected from xanthopterin; 2-aminopyrimidine hydrochloride; 2-aminopyrimidine hydrobromide; 6-hydroxy-2,4,5-triaminopyrimidine sulphate; 2,4-diamino-6-hydroxypyrimidine and nitroguanidine.
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7. A process according to any one of claims 1 to 5 wherein the liquid composition comprises at least one nitrogen-containing heterocyclic compound selected from 2,4,6-tris(2-pyridyl)-s-triazine; α , α' , α'' -tripyridyl; 1,10-phenanthroline; 4,7-diphenyl-1,10-phenanthroline; 4,7-dimethyl-1,10-phenanthroline; 4,7-diphenyl-1,10-phenanthroline disulphonic acid disodium salt; 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine; α , α' -dipyridyl; Phthalocyanine Green and 2,4-dimethylimidazole.
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8. A process according to any one of claims 1 to 5 wherein the liquid composition comprises at least one organic compound selected from 8-azaguanine; xanthopterin; 5-aminoindazole; 2-aminopyrimidine hydrochloride; 2-aminopyrimidine hydrobromide; benzoguanamine; acriflavine hydrochloride; 5-amino-1H-tetrazole; 6-amino-2-phenyl-4-quinolinol; 2-amino-6,8-dihydroxypurine; 2-aminopyrimidine; 6-hydroxy-2,4,5-triaminopyrimidine sulphate; 2,4-diamino-6-hydroxypyrimidine; 2-amino-4-hydroxy-6-methylpyrimidine; 4,6-dihydroxypyrimidine; nitroguanidine; 1-hydroxy-1H-benzotriazole monohydrate; 2-hydroxybenzimidazole and 2-amino-3-hydroxypyridine.
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Revendications



1. Un procédé comprenant le traitement d'une surface de conducteur en cuivre avec une composition liquide comprenant:
 - (I) des ions cuivre, un agent complexant des ions cuivre, un agent réducteur des ions cuivre, un agent d'ajustement du pH, de l'eau et
 - 5 (II) au moins un composé organique azoté, choisi parmi 2,4,6-tris-(2-pyridyl)-s-triazine, α,α',α'' -tripyridyle, 1,10-phénanthroline, 4,7-diphényl-1,10-phénanthroline, 4,7-diméthyl-1,10-phénanthroline, sel disodique d'acide 4,7-diphényl-1,10-phénanthroline-disulfonique, 3-(2-pyridyl)-5,6-diphényl-1,2,4-triazine, α,α' -dipyridyle, vert de phthalocyanine, 2,4-diméthyl-imidazoline, 8-azaguanine, xanthoptérine, 5-aminoindazole, chlorhydrate de 2-aminopyrimidine, bromhydrate de 2-aminopyrimidine, benzoguanamine, chlorhydrate d'acridine, 5-amino-1H-tétrazole, 6-amino-2-phényl-4-quinolinol, 2-amino-6,8-dihydroxypurine, 2-aminopyrimidine, sulfate de 6-hydroxy-2,4,5-triaminopyrimidine, 2,4-diamino-6-hydroxypyrimidine, 2-amino-4-hydroxy-6-méthylpyrimidine, 4,6-dihydroxypyrimidine, nitroguanidine, monohydrate de 1-hydroxy-1H-benzotriazole, 2-hydroxybenzimidazole et 2-amino-3-hydroxypyridine, la formation d'une couche de dépôt chimique de cuivre ayant un taux moyen d'absorption de la lumière de 0,5 ou plus pour une lumière de 300 à 800 nm, convertie à des valeurs permettant de retrouver la distribution d'intensité de la lumière solaire en fonction de la longueur d'onde, et la liaison d'une résine à la couche de dépôt chimique de cuivre.
2. Procédé selon la revendication 1, dans lequel la couche de dépôt chimique de cuivre a un taux d'absorption moyen de 0,7 ou plus.
3. Procédé selon la revendication 1 ou la revendication 2, dans lequel la composition liquide comprend 1 à 500 mg/l du composé organique azoté.
- 25 4. Procédé selon l'une quelconque des revendications précédentes, qui comprend de plus un traitement de la couche de dépôt chimique de cuivre avec au moins une solution parmi de l'ammoniac, une solution aqueuse contenant un agent réducteur et une solution acide, avant de lier une résine à la couche.
- 30 5. Procédé selon l'une quelconque des revendications 1 à 4, qui comprend de plus la liaison d'autres couches de résine au métal dont la surface est traitée, pour obtenir un stratifié à une ou plusieurs couches métalliques et plus d'une couche de résine.
- 35 6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel la composition liquide comprend au moins un composé organique azoté choisi parmi xanthoptérine, chlorhydrate de 2-aminopyrimidine, bromhydrate de 2-aminopyrimidine, sulfate de 6-hydroxy-2,4,5-triaminopyrimidine, 2,4-diamino-6-hydroxypyrimidine et nitroguanidine.
- 40 7. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel la composition liquide comprend au moins un composé hétérocyclique azoté choisi parmi 2,4,6-tris-(2-pyridyl)-s-triazine, α,α',α'' -tripyridyle, 1,10-phénanthroline, 4,7-diphényl-1,10-phénanthroline, 4,7-diméthyl-1,10-phénanthroline, sel disodique d'acide 4,7-diphényl-1,10-phénanthroline-disulfonique, 3-(2-pyridyl)-5,6-diphényl-1,2,4-triazine, α,α' -dipyridyle, vert de phthalocyanine, 2,4-diméthylimidazole.
- 45 8. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel la composition liquide comprend au moins un composé organique choisi parmi 8-azaguanine, xanthoptérine, 5-aminoindazole, chlorhydrate de 2-aminopyrimidine, bromhydrate de 2-aminopyrimidine, benzoguanamine, chlorhydrate d'acridine, 5-amino-1H-tétrazole, 6-amino-2-phényl-4-quinolinol, 2-amino-6,8-dihydroxypurine, 2-aminopyrimidine, sulfate de 6-hydroxy-2,4,5-triaminopyrimidine, 2,4-diamino-6-hydroxypyrimidine, 2-amino-4-hydroxy-6-méthylpyrimidine, 4,6-dihydroxypyrimidine, nitroguanidine, monohydrate de 1-hydroxy-1H-benzotriazole, 2-hydroxybenzimidazole et 2-amino-3-hydroxypyridine.
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Ansprüche

- 55 1. Verfahren zur Behandlung einer Kupferleiter-Oberfläche, dadurch gekennzeichnet, daß mit einer flüssigen Zusammensetzung, die
 - (I) Kupferionen, ein Komplettierungsmittel für Kupferionen, ein Reduktionsmittel für Kupferionen, ein



Mittel zur Einstellung des pH-Wertes, Wasser und

(II) mindestens eine Stickstoff enthaltende organische Verbindung, ausgewählt unter 2,4,6-Tris-(2-pyridyl)-s-triazin, α,α',α'' -Tripyridyl, 1,10-Phenanthrolin, 4,7-Diphenyl-1,10-phenanthrolin, 4,7-Dimethyl-1,10-phenanthrolin, 4,7-Diphenyl-1,10-phenanthrolin-disulfonsäure-dinatriumsalz, 3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazin, α,α' -Dipyridyl, Phthalocyaningrün, 2,4-Dimethylimidazolin, 8-Azaguanin, Xanthopterin, 5-Aminoindazol, 2-Aminopyrimidin-hydrochlorid, 2-Aminopyrimidin-hydrobromid, Benzoguanamin, Acriflavinhydrochlorid, 5-Amino-1H-tetrazol, 6-Amino-2-phenyl-4-chinolinol, 2-Amino-6,8-dihydroxypurin, 2-Aminopyrimidin, 6-Hydroxy-2,4,5-triaminopyrimidinsulfat, 2,4-Diamino-6-hydroxypyrimidin, 2-Amino-4-hydroxy-6-methylpyrimidin, 4,6-Dihydroxypyrimidin, Nitroguanidin, 1-Hydroxy-1H-benzotriazol-monohydrat, 2-Hydroxybenzimidazol und 2-Amino-3-hydroxypyridin, enthält, stromfrei eine Kupferabscheidungsschicht mit einer durchschnittlichen Lichtabsorptionsrate von 0,5 oder mehr unter Verwendung eines Lichts von 300 bis 800 nm und umgewandelt auf Werte, so daß die Wellenlängen-Intensitätsverteilung von Sonnenlicht erfüllt wird, gebildet wird und ein Harz mit der stromfrei abgeschiedenen Kupferschicht verbunden wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die stromfrei abgeschiedene Kupferschicht eine durchschnittliche Absorptionsrate von 0,7 oder darüber besitzt.
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die flüssige Zusammensetzung von 1 bis 500 mg/l der Stickstoff enthaltenden organischen Verbindung enthält.
4. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß zusätzlich die stromfrei abgeschiedene Kupferschicht mit mindestens einer Lösung aus der Gruppe Ammoniak-Wasser, einer wäßrigen Lösung, die ein Reduktionsmittel enthält, und einer Säure-Lösung vor dem Verbinden des Harzes mit der Schicht behandelt wird.
5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß weitere Harzschichten mit dem Metall, dessen Oberfläche behandelt wurde, verbunden werden, so daß ein Laminat aus einer oder mehreren Metallschichten und mehr als einer Harzschicht erhalten wird.
6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die flüssige Zusammensetzung mindestens eine Stickstoff enthaltende Verbindung, ausgewählt aus der Gruppe Xanthopterin, 2-Aminopyrimidin-hydrochlorid, 2-Aminopyrimidin-hydrobromid, 6-Hydroxy-2,4,5-triaminopyrimidinsulfat, 2,4-Diamino-6-hydroxypyrimidin und Nitroguanidin, enthält.
7. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die flüssige Zusammensetzung mindestens eine Stickstoff enthaltende heterocyclische Verbindung, ausgewählt unter 2,4,6-Tris-(2-pyridyl)-s-triazin, α,α',α'' -Tripyridyl, 1,10-Phenanthrolin, 4,7-Diphenyl-1,10-phenanthrolin, 4,7-Dimethyl-1,10-phenanthrolin, 4,7-Diphenyl-1,10-phenanthrolin-disulfonsäure-dinatriumsalz, 3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazin, α,α' -Dipyridyl, Phthalocyaningrün und 2,4-Dimethylimidazolin, enthält.
8. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die flüssige Zusammensetzung mindestens eine organische Verbindung, ausgewählt unter 8-Azaguanin, Xanthopterin, 5-Aminoindazol, 2-Aminopyrimidin-hydrochlorid, 2-Aminopyrimidin-hydrobromid, Benzoguanamin, Acriflavinhydrochlorid, 5-Amino-1H-tetrazol, 6-Amino-2-phenyl-4-chinolinol, 2-Amino-6,8-dihydroxypurin, 2-Aminopyrimidin, 6-Hydroxy-2,4,5-triaminopyrimidinsulfat, 2,4-Diamino-6-hydroxypyrimidin, 2-Amino-4-hydroxy-6-methylpyrimidin, 4,6-Dihydroxypyrimidin, Nitroguanidin, 1-Hydroxy-1H-benzotriazol-monohydrat, 2-Hydroxybenzimidazol und 2-Amino-3-hydroxypyridin, enthält.