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DESCRIPTION

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PROCESS FOR ELECTROPLATING NONCONDUCTIVE SURFACE

The present invention relates to a process for electroplating a nonconductive surface, and, more particularly, to a process for directly electroplating a conductive metal to the inner walls of through-holes in printed-wiring boards.

In printed-wiring boards such as double-sided boards and multilayer boards, through-holes are provided in the substrate. The inner walls of the through-holes are electroplated with a conductive metal in order to secure conductivity among the circuits.

As a method of electroplating the nonconductive inner walls of through-holes, Shortt et al. disclose a method of electroplating after making the through-hole inner walls with electro-conductive by the application of particles of silver, copper, graphite, or the like (USP 3,163,588). In this method, however, defects such as pinholes are created in the plated layer of the through-hole inner wall, when the excess of conductive layer has been removed. This inner wall must be re-electroplated, which not only makes the process complicated, but also it cannot be applied at all to the manufacture of the reliable high density printed-wiring boards currently required.

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Radovsky et al., in the discussion of several drawbacks of graphite as a conductive layer for electroplating, indicate that graphite provides only weakly attached electroplated conductive metal and produces electroplated through-holes with uneven diameters. Radovsky et al. also indicate that graphite itself possesses only a small electric resistance (USP 3,099,608).

At the present time, electroless copper plating is applied as the metal plating of through-hole inner wall. However, electroless copper plating has the following drawbacks; (1) it requires a comparatively long period of time, (2) a number of baths must be monitored all the time during the plating process (required components must be supplied to each bath and sufficient care must be taken so that the baths are not contaminated with components used in the preceding steps, because the baths are extremely sensitive to contamination), (3) a number of washing baths are needed, consuming a great quantity of water for washing, and (4) waste water disposal is expensive.

As a method for electroplating without using the electroless copper plating having these drawbacks, Randolph et al. propose a method of electroplating after forming a carbon black layer by applying a dispersion of carbon black having an average diameter of less than



about 3 μm to the through-hole inner wall and a surfactant, and further forming over this carbon black layer a graphite layer by applying a dispersion of graphite having an average diameter of less than about 1.5 μm and a surfactant (USP 5,139,642). This method requires formation of two layers, a carbon black layer and a graphite layer, as base layers for electroplating, resulting in complicated processes and increased cost.

The present inventors have undertaken extensive studies and have found that a method of electroplating a conductive metal over a nonconductive surface, especially over the through-hole inner wall of printed-wiring board, can afford higher reliability than the method of providing two layers, a carbon black layer and a graphite layer, as base layers for electroplating, and can achieve the object at a lower cost.

Accordingly, an object of the present invention is to provide a process for electroplating a nonconductive surface comprising,

providing an aqueous dispersion containing graphite with an average particle diameter of 2 μm or less and a binder (hereinafter referred to as "specific graphite aqueous dispersion"),

applying the specific graphite aqueous dispersion over a nonconductive surface to attach graphite



particles, thus forming a graphite layer, and
electroplating using the graphite layer as a
conductive layer.

Another object of the present invention is to
provide a process for electroplating a through-hole inner
wall of a printed-wiring board which comprises,

providing the specific graphite aqueous dispersion,
applying the specific graphite aqueous dispersion
over a surface of a substrate with conductive metal
layers laminated over the surface thereof and through-
holes provided therethrough, to attach graphite
particles, thus forming a graphite layer,

removing the graphite layer attached to the surface
of the conductive metal layers by etching these metal
layers for a thickness of 0.01 to 1.8 μm , and

electroplating using the graphite layer as a
conductive layer.

In the process of the present invention, the
specific graphite aqueous dispersion is first applied
over the nonconductive surface to be electroplated to
attach graphite particles and form a graphite layer.

The graphite particles are super fine particles with
an average diameter of 2 μm or less, preferably 1 μm or
less, and more preferably 0.7 μm or less. If the average
diameter is greater than 2 μm , not only the conductivity
is lowered, but also the attachability of a conductive



metal to be electroplated to the nonconductive surface is poor.

The amount of graphite particles in the specific graphite aqueous dispersion is preferably less than 6% by weight (% by weight is hereinafter simply referred to as %), and more preferably 2% to 5%. If this amount is greater than 6%, the attachability of a conductive metal to be electroplated to the nonconductive surface is poor; if less than 2%, the graphite particle density in the graphite layer is too small for the material to be sufficiently conductive.

Either organic or inorganic binders can be used as the binder for preparing the specific graphite aqueous dispersion. Inorganic binders, for example sodium silicate and potassium silicate, are preferred in order to firmly attach the graphite particles to the inside of the through-holes.

The amount of binder contained in the specific graphite aqueous dispersion is usually in the range of 0.05 to 5%. If the amount of the binder is too great, conductivity and film-forming capability are decreased.

Incorporation of a water-soluble polymer, such as carboxymethyl cellulose, starch, and gum arabic, is preferable for promoting stability of the specific graphite aqueous dispersion. Furthermore, the specific

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graphite aqueous dispersion is preferably adjusted to about pH 9-13 by the addition of ammonia, sodium hydroxide, or potassium hydroxide. The addition of ammonia is particularly preferred. Further, it is desirable to add an anionic surfactant of carboxylic acid-type, polycarboxylic acid-type, or the like in order to increase the attachability.

In preparing the specific graphite aqueous dispersion, wet pulverization, dispersion, and classification are preferably employed for improving dispersion stability and narrowing the size distribution of the graphite particles.

Factors generally required for paints are the capability of wetting the substrate, sufficient fluidity to produce a uniform film, the exhibition of good attachability when drying, and the capability of reserving a continuous and complete film. These characteristics are required also for the specific graphite aqueous dispersion to form a graphite layer in the through-hole internal walls. The use of the specific graphite aqueous dispersion having these characteristics produces a uniform graphite film in the through-hole internal walls and ensures formation of a metallic layer which is free from defects by electroplating.

There are no specific limitations as to the method for forming a graphite layer over a nonconductive



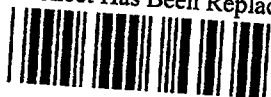
surface. An example of a preferable method is to apply the specific graphite aqueous dispersion over the nonconductive surface by spraying, dipping, or coating, and then removing the dispersion medium by air-blowing or placing in an oven.

A conductive metal is then electroplated using the graphite layer as a conductive layer.

There are no specific limitations as to the method of electroplating. For example, the electroplating can be carried out at a normal temperature and 1.5 to 3 A/dm² for 60 to 90 minutes in a common electroplating bath. There are also no specific limitations to the conductive metal used for the electroplating. Copper and nickel are given as examples.

The process of the present invention can be applied to electroplating of various nonconductive materials. It is particularly useful for electroplating through-hole inner walls of printed-wiring boards made of, for example, paper-based phenol resin copper laminated boards, glass-based epoxy resin copper laminated boards, composite copper laminated boards, polyimide copper laminated boards, fluorine-containing resin copper laminated boards, and copper laminated boards for flexible circuits. Since attachability using the electroplating method of the present invention is

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excellent, it can produce evenly attached and highly reliable electroplating over even internal walls of through-holes, called viaholes, which are holes with a diameter of 0.3 to 0.5 mm.

Typical steps adopted for applying electroplating using the process of the present invention over through-hole internal walls of a printed-wiring board are now illustrated taking the case where electroplating is performed over through-hole internal walls of a substrate with copper foils laminated over the surface thereof (a glass-based epoxy resin copper laminated board).

(1) Washing of substrate surface

This is a treatment to clean the through-hole inner walls, and comprises washing the board with a weak alkaline solution of about pH 9-12 containing an anionic surfactant such as a phosphoric acid ester at 35-65°C for about 20 to 60 seconds and rinsing with water.

(2) Conditioning treatment

This is a treatment to accelerate attachment of graphite particles to the cleaned through-hole inner walls, and normally comprises treating with a weak alkaline solution of about pH 9-12 containing a cationic surfactant of polyamine-type, polyamide-type, or the like at 20-60°C for about 20 to 60 seconds, and rinsing with water.

(3) Application of graphite particle



Immerse the board in the specific graphite aqueous dispersion, normally, at 20-60°C for about 30 to 90 seconds.

(4) Removal of aqueous medium

The board is blown with air at 30-60°C for about 30 to 90 seconds.

(5) Microetching

This is a step for removing the graphite layer on the copper surface. Among the graphite layer attached to the copper surface and that attached to the non-conductive surface in the through-hole inner walls, the former decreases attachability of the conductive metal to be electroplated to the copper surface and impairs the conductivity between the copper surface and the conductive metal. For this reason, the graphite layer on the copper surface must be removed. In this treatment, graphite particles are removed by etching the copper surface beneath the graphite layer without effecting any action on the graphite itself. This treatment can be carried out, for example, by dipping the substrate in an etching solution of the sulfuric acid-hydrogen peroxide type at a temperature of 20-30°C to etch to an approximate thickness of 0.01-1.8 μm , preferably 0.1-1.2 μm , followed by washing and drying. If the depth of etching is less than 0.01 μm , graphite particles remain

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on the copper surface; if overetched in excess of 1.8 μm , the conductivity between the copper and the graphite layer on the nonconductive surface is lost and electroplate voids tend to be produced.

(6) Electroplating

Electroplating can be carried out under conditions of normal temperature and at 1.5 to 3 A/dm^2 for 60-90 minutes in a common electroplating bath.

Electroplating with a exceptionally high reliability can be performed if the above steps (2)-(4) are repeated, in which case these steps are carried out in the order of (1), (2), (3), (4), (2), (3), (4), (5) and (6).

It is possible to combine said step (1) (washing of substrate surface) and step (2) (conditioning treatment). In this instance, the board may be treated with a weak alkaline solution of about pH 9-12 containing a cationic surfactant of polyamine-type, polyamide-type, or the like and a solvent such as ethanolamine 20-60°C for about 20 to 60 seconds and rinsed with water.

Other features of the invention will become apparent in the course of the following description of the exemplary embodiments which are given for illustration of the invention and are not intended to be limiting thereof.

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EXAMPLES

Example 1

A substrate (10 x 25 cm) consisting of an insulating layer of glass impregnated with epoxy resin and copper foils with a thickness of 35 μ m laminated on both sides of the insulating layer, provided with about 960 through-holes with a diameter of 0.3 to 0.8 mm was processed as follows.

The substrate was dipped into a solution consisting of 0.5% cationic surfactant, 1.0% of amine, and water (a cleaner conditioner) at 45°C for 40 seconds, followed by washing with water. The substrate was then dipped into a graphite dispersion consisting of 4% of graphite particles having an average particle diameter of 0.4 μ m, 0.5% of carboxymethyl cellulose, 0.5% of sodium silicate, 1% of a cationic surfactant, and water, adjusted to pH 10, at 25°C for 60 seconds, followed by blowing air at 40°C for 45 seconds to remove a dispersion medium. The substrate was again dipped into the cleaner conditioner at 25°C for 40 seconds and washed, then into the graphite dispersion at 25°C for 60 seconds, followed by blowing air at 40°C for 45 seconds to remove the dispersion medium. To perform microetching, this substrate was dipped into a liquid comprising sulfuric acid and hydrogen peroxide (CA-90: trademark, a product of MEC Co.) at 25°C for 20 seconds, followed by washing with



water and drying. Copper was removed to a thickness of 1 μm by this microetching treatment.

Next, electroplating was performed using the substrate under conditions of normal temperature and at 2 A/dm^2 for 90 minutes using a conventional copper plating bath.

As a result of a backlight test, it was found that a uniform copper electroplated layer had been provided over the walls of the through-holes and there were no voids in any through-holes, including those having a comparatively large a diameter of 0.6 to 0.8 mm and those having a small diameter of 0.3 to 0.5 mm. Further, the adhesion was evaluated by the thermal stress test (conforming to JIS C 5012, except that solder at a temperature of 260-265°C was used instead of oil and the test was carried out at 10 cycles) to confirm that there was no electroplated copper released from the through-hole walls.

Example 2

The same substrate as used in Example 1 was treated and electroplated in the same manner as in Example 1, except that the content of graphite particles in the graphite aqueous dispersion was 3.0%.

The electroplated substrate was evaluated in the same manner as in Example 1 to confirm that the substrate



was excellently electroplated with a uniform thickness copper layer with no voids in any through-holes, including those having a small diameter of 0.3 to 0.5 mm. Also, no release of electroplated copper from the walls of the through-holes was found as a result of the adhesion test.

Example 3

A substrate was treated and electroplated in the same manner as in Example 1, except that a graphite dispersion consisting of 3% of graphite particles having an average particle diameter of 0.4 μm , 0.5% of potassium silicate, 1% of a cationic surfactant, and water, and adjusted to pH 10, was used.

The electroplated substrate was evaluated in the same manner as in Example 1 to confirm that the substrate was excellently electroplated with a uniform thickness copper layer with no voids in any through-holes, including those having a small diameter of 0.3 to 0.5 mm. Also, no release of electroplated copper from walls of through-holes was found as a result of the adhesion test.

Example 4

A substrate was treated and electroplated in the same manner as in Example 1, except that a graphite dispersion containing 4.5% of graphite particles having an average particle diameter of 0.5 μm was used.

The electroplated substrate was evaluated in the



same manner as in Example 1 to confirm that the substrate was excellently electroplated with a uniform thickness copper layer with no voids in any through-holes, including those having a small diameter of 0.3 to 0.5 mm. Also, no release of electroplated copper from the walls of the through-holes was found as a result of the adhesion test.

Comparative Example 1

A substrate was treated and electroplated in the same manner as in Example 1, except that a graphite dispersion containing 3.0% of graphite particles having an average particle diameter of 3 μ m was used.

The electroplated substrate was evaluated in same manner as in Example 1. Voids were found in about 70% of the through-holes having a diameter of 0.6 to 0.8 mm and in almost all through-holes having a diameter of 0.3 to 0.5 mm. The adhesion test was carried out on through-holes having a diameter of 0.8 mm or larger. Copper electroplated inside the holes had peeled off, revealing that the product was unacceptable.

Comparative Example 2

A substrate was treated and electroplated in the same manner as in Example 1, except that a graphite dispersion containing 4.5% of graphite particles having an average particle diameter of 3 μ m was used.

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The electroplated substrate was evaluated in same manner as in Example 1. Voids were found in about 50% of through-holes having a diameter of 0.6 to 0.8 mm and in almost all through-holes having a diameter of 0.3 to 0.5 mm. The adhesion test was carried out on through-holes having a diameter of 0.8 mm or larger. Copper electroplated inside the holes had peeled off, revealing that the product was unacceptable.

These results shows that according to the process of the present invention copper can be excellently electroplated with strong adhesion to the through-hole walls as compared with the case where a graphite aqueous dispersion containing graphite particles having an average diameter of larger than 2 μ m is used.

As illustrated above, the process of the present invention ensures reliable electroplating on nonconductive surfaces at a low cost. This process is highly reliable and can be applied with advantage especially to multi-layered, small diameter printed-wiring boards.

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CLAIMS

1. A process for electroplating a nonconductive surface comprising,
providing an aqueous dispersion containing graphite with an average particle diameter of 2 μm or less and a binder,
applying said graphite aqueous dispersion of graphite particles over a nonconductive surface to attach graphite particles, thus forming a graphite layer, and
electroplating using the graphite layer as a conductive layer.
 2. A process for electroplating a through-hole inner wall of a printed-wiring board which comprises,
providing an aqueous dispersion containing graphite with an average particle diameter of 2 μm or less and a binder,
applying said aqueous dispersion of graphite particles over a surface of a substrate with conductive metal layers laminated over the surface thereof and through-holes provided therethrough, to attach graphite particles, thus forming a graphite layer,
removing the graphite layer attached to the surface of the conductive metal layers by etching these metal layers for a thickness of 0.01 to 1.8 μm , and
electroplating using the graphite layer as a conductive layer.
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