

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN AND RELATING TO PRINTED CIRCUIT BOARD MATERIALS

(71) We, THE MICA CORPORATION, of 4031 Elenda Street, Culver City, California 90230, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to printed circuit board materials and to methods of etching such materials.

United States Patent No. 2,662,957 (Eisler) describes a printed circuit board material consisting of an insulating support, one or more layers of resistance material, and an outer layer of highly conductive material. Printed circuits can be made from this stock. Essentially, the method of converting the stock into the desired product comprises the selective removal of unwanted layers, to leave areas having the required electrical properties, namely, insulating areas (all layers above the support removed), resistance areas (the conductive layer removed), and conductive areas (no layers removed).

Eisler discloses the following resistive layers: An alloy of manganese (over 80%) and copper heat treated to over 600 degrees C.; certain copper-manganese-nickel alloys; copper-nickel alloys; nickel-silver (i.e. alloys of copper, nickel and zinc); copper-silicon; copper-nickel-chromium; chromium-nickel; and chromium-nickel-iron. Some alloys of noble metals are also disclosed, for example silver-palladium.

We have found that conventional resistive materials do not always form good bond to the support. While not bound by any theory, it appears that the support, which is usually an organic resin such as epoxy, polyamide, etc., and the resistive material form a heterogeneous interface which provide a mere mechanical bond or interlock.

The invention provides a printed circuit board material in the form of a multilayer stock comprising an insulating support, at least one layer of electrical resistance material adhering to said support, and a layer of a highly conductive material adhering to a layer of the resistance material and in intimate contact therewith, the layer of electrical resistance material that adheres to said support comprising electroplated nickel-phosphorus.

It has been surprisingly found that a better bond characterised by greater resistance to peel is formed when the layer of the resistive material that adheres to the support comprises electroplated nickel-phosphorus. Improved temperature stability of the resistive layer and higher resistance values per unit area of the printed circuit board material can be attained in accordance with the invention.

We have also found that the present invention provides numerous advantages over resistive layers obtained by the use of electroless baths. The electroless baths are metastable and autocatalytic, and are characterised by poor reproducibility. Further, the unit resistivity is limited by the amount of phosphorus obtainable in deposits from such baths. The electroplating bath is quite reproducible, and can readily provide up to about 30% by weight phosphorus in the deposit. The deposit composition can be regulated by varying the current density. The electroplating bath is far less temperature sensitive than the electroless bath. In fact, in the electroplating bath, the deposit composition is independent of the temperature (only the deposition rate being affected), whereas in the electroless bath the deposit composition is a function of temperature.

It is anticipated that this invention, representing a significant advance in the art, will be widely adopted by fabricators of

printed circuits.

The layer of electrical resistance material that adheres to said support may comprise electroplated nickel-phosphorus containing up to about 30% by weight of phosphorus. The phosphorus content is critical in a practical and technical sense insofar as this invention is concerned. The preferred phosphorus content has been found to be from about 8% to 30% by weight.

Advantageously, a major portion of the oxides, hydroxides and/or peroxides of nickel are formed on the surface that is adjacent to the support of the layer of electrical resistance material that adheres to the support. Such resistive materials seem to have a greater affinity for the resin of the support. In fact, the bond appears to be of a fundamentally different type as compared with previously proposed printed circuit boards as in Eisler's United States Patent Specification. The nickel material of this invention appears to produce an electrical and/or chemical adhesion of the resistance layer to the support. In addition, we have found that the resistive material has improved high temperature stability and higher resistivity per unit area is attainable. Preferably, the said oxides, hydroxides and/or peroxides are produced by electrolytic formation.

The layer of electrical resistance material that adheres to said support may be electroplated onto the layer of highly conductive material. The layer of highly conductive material is preferably uppermost in the multi-layer stock.

The highly conductive layer of the stock preferably consists of a pre-formed metal foil such as copper foil, tinned copper foil, aluminium foil, zinc foil or silver foil, and any convenient foil thickness may be used, for instance 0.002".

Various materials may be used for the insulating support. For example, the support may be polyamide such as those based on organic diamines and dicarboxylic or tetracarboxylic acids. The epoxy resins based on the polyglycidyl ethers of organic polyphenols are also preferred. These resinous supports may contain reinforcing materials such as fiberglass fabric. The support can also be phenolic resin-impregnated paper, melamine resin-impregnated paper, or polyester resin containing chopped glass reinforcement.

The removal of a nickel-phosphorus layer in a printed circuit board material having copper and nickel or nickel-phosphorus layers, without the removal of copper, may be accomplished by removing the nickel-phosphorus layer with an aqueous solution of ferric sulphate and sulphuric acid. Preferably ferric sulphate and sulphuric acid in aqueous solution are used;

the solution may be about six molar sulphate ion.

The disclosure of United States Patent Specification No. 3 743 583 (Serial No. 106,832 filed 15th January 1971) is incorporated herein by reference.

A printed circuit board material and a method of etching the same in accordance with the invention will now be described in detail, by way of example.

The preferred electroplating bath used for this purpose has the following composition:

	g/l	M/l	
Nickel sulfate hexahydrate	37.50	0.143	80
Nickel chloride hexahydrate	11.25	0.048	
Nickel carbonate	7.12	0.060	
Phosphoric acid (as 100% acid)	12.25	0.125	85
Phosphorous acid	7.50	0.092	
Dowfax (Trade Mark) 2A1	0.11 ml	—	
Water	Make up to one litre		
Concentration of nickel ion in mols per litre	—	0.25	90

The phosphoric acid and phosphorous acid content may be adjusted, or even reduced to zero to provide from 0 to 30% by weight phosphorus in the resistive deposit. The more typical composition, however, is from 8 to 30% by weight of phosphorus.

The resistive layer is prepared by the electroplating of nickel-phosphorus onto a conductive layer, which is typically a conductive metal foil.

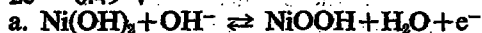
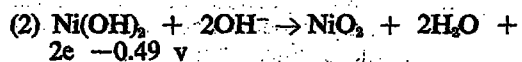
The anode typically, although not necessarily, is a 7" x 11" one ounce per square foot electrolytically deposited nickel foil laminated to a 1/16" thick epoxy fiberglass board. The anode may also be an inert material such as carbon or graphite, in which case no nickel is present in the anode. The cathode is preferably electrolytic copper foil or other material suitable as the conductive layer.

The nickel oxide, hydroxide and/or peroxide is normally formed by treating the bimetallic strip comprising the conductive layer and the resistive material including nickel in an electroformation process, that is, an electrolytic formation process. The nickel oxide, hydroxide and/or peroxide is electrolytically formed on the resistive material and so is produced predominantly at the exposed surface of the resistive material in the bimetallic strip. The bulk of the nickel-phosphorus within the resistive layer is not chemically altered by the electroforming process. The first step of electroformation can be represented as follows:



The base is normally provided by a strong alkali such as potassium hydroxide.

In a second step, the following reaction occurs:



Actually a mixture of Ni^{+2} and Ni^{+4}

After the electroforming, the double layer foil is laminated, nickel oxide, hydroxide and/or peroxide side at the interface, with several plies of fiberglass fabric pre-impregnated with an appropriate formulation of curable organic resins. The lamination process is well known to those skilled in the art. Following lamination, and at the time of use in printed circuit manufacture, the copper surface is coated with photoresist. The layer of photoresist is then exposed through a photographic negative containing the negative image of the combined resistor and conductor patterns. The exposed resist is developed, and the unexpected portion washed away. The panel with the developed image is then etched in an etchant such as an alkaline etchant or ferric chloride acidified with hydrochloric acid until the bare copper is removed. The panel is then rinsed in water and immersed in an acid etchant as more fully hereinafter described until the bare nickel-phosphorus is removed. The remaining exposed photoresist is stripped off and the panel is coated with a new layer of photoresist. This layer is exposed through a photographic negative containing the negative image of the conductor pattern. The exposed resist is developed, and the unexposed portion washed away. The panel with the developed image is then etched in a chromic acid etchant as more fully described below until the bare copper is removed. The panel is then rinsed in water and dried. At this point, the conductive and resistive patterns are individually defined, and in appropriate electrical contact with each other.

The general procedure as detailed here and further in the example which follows contemplates the use of photographic negatives and negative working resists. It should be noted specifically that other processing materials are also suitable. For instance, photographic positives can be used in combination with positive working resists (e.g. PR-102 by General Aniline & Film Corporation). Silk screening techniques can also be used in conjunction with any resist that is not attacked by the etchants.

The following example is presented solely to illustrate the invention and should not be regarded as limiting in any way.

EXAMPLE

The shiny or drum side of copper foil is coated with a strippable vinyl coating. The copper is cut to the size. The plating bath, made up as previously indicated, is heated to 170 degrees F. with constant agitation. A nickel anode is mounted in its vertical holder brace and attached to the power supply. The copper is immersed in 20 percent hydrochloric acid for 3 minutes, and then rinsed twice in distilled water. The copper is fastened to an electrode backup plate. The copper cathode assembly is mounted in its vertical holder brace in the bath, and the agitation is stopped. The power supply is attached to the protruding copper strip and the cathode assembly is allowed two minutes to equilibrate with the temperature of the bath. The power supply, having been preadjusted for the desired current and voltage is turned on for the appropriate plating period and then turned off, in this case a current density of 1.08 amps per square decimeter for 60 seconds gives a sheet resistivity of 50 ohms per square. The bath is allowed to stand one minute before removing the cathode assembly. The cathode assembly is taken apart and the now plated copper foil separated. The copper foil is rinsed first in tap water, then in distilled water at 190 degrees F. The plated foil is dried in a stream of warm air. The foil is then placed in an electroforming bath containing a 30% solution of KOH. The plated foil, plated side down is stacked atop several layers of fiberglass fabric, pre-impregnated with an appropriate formulation of epoxy resins. The assemblage is cured in a stream heated hydraulic press under heat and pressure to produce an epoxy-fiberglass laminate, clad on one or both sides with the plated foil made as described above. The copper surface of the panel is coated with photoresist (Kodak KPR). The photoresist is exposed through a photographic negative of the combined conductor and resistor patterns. The resist is developed and the unexposed portions washed away. The panel is immersed in an alkaline etchant such as MacDermid's MU to remove the copper in the areas not covered by photoresist. The panel is immersed in an acid etchant to remove the exposed resistive material. This etchant has the following composition:

$\text{Fe}_2(\text{SO}_4)_3 \cdot \text{XH}_2\text{O}$ [(containing 75% by weight anhydrous $\text{Fe}_2(\text{SO}_4)_3$)]	535 gms	125
Concentrated H_2SO_4	200 ml	
H_2O	to 1 litre	

The etchant is essentially passive to copper.

The panel is rinsed in water, the remaining photoresist stripped off, and a new layer of photoresist applied. The photoresist is exposed through a photographic negative of the conductor pattern. The resist is developed and the unexposed portions washed away. The panel is immersed in an etchant to remove the copper in the areas not covered by photoresist. This etchant has the following composition:

Chromic Acid (As CrO_3)	300 gms
Concentrated H_2SO_4	35 ml
H_2O	to 1 litre

This etchant is essentially passive to the resistive material.

The panel is rinsed in water and the remaining photoresist stripped off. The resistor-conductor pattern is now complete.

The time required to convert the nickel to the oxide, hydroxide and/or peroxide at constant potential is independent of the area of the electrodes and the current level. It has also been found that a greater depth of conversion results by the cycling of the current to the plated foil, that is, by repetitious charging and discharging.

WHAT WE CLAIM IS:—

1. A printed circuit board material in the form of a multilayer stock comprising an insulating support, at least one layer of electrical resistance material adhering to said support, and a layer of a highly conductive material adhering to a layer of the resistance material and in intimate contact therewith, the layer of electrical resistance material that adheres to said support comprising electroplated nickel-phosphorus.

2. A printed circuit board material as claimed in claim 1, wherein the electroplated nickel-phosphorus contains up to about 30% by weight of phosphorus.

3. A printed circuit board material as claimed in claim 2, wherein the electroplated nickel-phosphorus contains from

about 8% to about 30% by weight of phosphorus.

4. A printed circuit board material as claimed in any one of claims 1 to 3, wherein a major portion of the oxides, hydroxides and/or peroxides of nickel are formed on the surface that is adjacent to the support of the layer of electrical resistance material that adheres to the support.

5. A printed circuit board material as claimed in claim 4, wherein said oxides, hydroxides and/or peroxides are produced by electrolytic formation.

6. A printed circuit board material as claimed in any one of claims 1 to 5, wherein the conductive layer comprises copper foil.

7. A printed circuit board material as claimed in any one of claims 1 to 6, wherein the support comprises a reinforced organic resin.

8. A printed board material as claimed in any one of claims 1 to 6, wherein the support comprises a fiberglass fabric reinforced epoxy resin.

9. A printed circuit board material as claimed in any one of claims 1 to 8, in which the layer of electrical resistance material that adheres to said support is electroplated on the layer of highly conductive material.

10. A printed circuit board material in the form of a multilayer stock substantially as hereinbefore described with reference to the Example.

11. A printed circuit made from a multilayer stock as claimed in any one of claims 1 to 10.

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The panel is rinsed in water, the remaining photoresist stripped off, and a new layer of photoresist applied. The photoresist is exposed through a photographic negative of the conductor pattern. The resist is developed and the unexposed portions washed away. The panel is immersed in an etchant to remove the copper in the areas not covered by photoresist. This etchant has the following composition:

Chromic Acid (As CrO_3)	300 gms
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4. A printed circuit board material as claimed in any one of claims 1 to 3, wherein a major portion of the oxides, hydroxides and/or peroxides of nickel are formed on the surface that is adjacent to the support of the layer of electrical resistance material that adheres to the support.

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9. A printed circuit board material as claimed in any one of claims 1 to 8, in which the layer of electrical resistance material that adheres to said support is electroplated on the layer of highly conductive material.

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