

EUROPEAN QUALIFYING EXAMINATION 1998

PAPER B CHEMISTRY

THIS PAPER COMPRISES:

- | | |
|-----------------------------------|-----------------|
| * DESCRIPTION OF THE APPLICATION | 98/B(C)/E/1-10 |
| * COMMUNICATION | 98/B(C)/E/11-12 |
| * DOCUMENT I (STATE OF THE ART) | 98/B(C)/E/13-15 |
| * DOCUMENT II (STATE OF THE ART) | 98B(C)/E/16-20 |
| * DOCUMENT III (STATE OF THE ART) | 98/B(C)/E/21-23 |

DESCRIPTION OF THE APPLICATION

In many applications, it is essential to provide strong adherence between a metallic surface and a polymeric surface. Examples of such applications are widely diversified. For example, the strong adherence of metal to polymer is critical in the manufacture of printed circuit boards in the electronics, telecommunications, computer and other industries. In principle, such a printed circuit board comprises
5 an electrically insulating substrate and - adhering to at least one of its surfaces - strip conductors made mostly of copper.

In the manufacture of electronic devices, such as computers, printed circuit boards are widely used to support discrete electronic components and to provide the electrical circuitry between the components.
10 The printed circuit boards of today are composite structures (laminates) having a central core. The core layer is typically a dielectric material such as a thermosetting resin, e.g. an epoxy or phenolic polyester resin, reinforced with glass fibres. This dielectric material is referred to in the art as a "prepreg". The prepreg has metallic circuitry applied on both sides, usually formed of a metal film layer such as copper. The metal film layer is etched or otherwise processed according to the art to provide circuits of
15 predetermined geometrical configuration. The discrete electronic components, such as resistors, capacitors and semiconductors, are mounted on the circuit board and electrically connected to the strip conductors or signal conductors or electric power tracks left over after the etching or other processing.

The printed circuit board may be a two-sided composite board having circuitry on both sides of the
20 dielectric layer (A-B-A sandwich structure), or it may be a laminated multi-layer board (A-B-A-B-...-A) which also contains internal layers of signal conductors and power tracks (A) separated by the dielectric layers (B). The laminated multi-layer printed circuit boards are prepared from individual circuit boards which are laminated to form the multi-layer structure having etched metal circuitry sandwiched between the prepreg layers. The laminated multi-layer boards are provided with perforations which allow for
25 connection of the circuit lines on the different metal layers. At these perforations an additional phenomenon, the so-called "haloing" or "pink ring", is often observed in the further processing. It is caused by the dissolution of oxidised copper (from etching) around the perforations by the action of acidic

aqueous solutions. This affects the bonding between the layers and hence the structure of the circuit board. Moreover, the reliability of electric contacts is often impaired due to bad quality of the soldering or other interconnections at the perforations having these pink rings.

- 5 Various methods have been employed for providing a metal film layer on one or both sides of a prepreg substrate. These methods, e.g. vacuum metallisation, are known in the art and need not be further explained here. When such metallised substrates are laminated to further polymeric prepreg substrates to form a multi-layer printed circuit board, the adhesion of the metal film layers such as copper, aluminium or silver to these further substrates is often inadequate, especially when the polymers are epoxy resins.

10

The preparation of such printed circuit boards is generally known in the art, and the present invention pertains exclusively to an improvement of the bonding strength between the metal foil or strip conductors and the substrate of the composite board in order to prevent partial or total disintegration of the laminated electrical circuitry, e.g. during the etching, chemical cleaning or soldering steps of the circuit boards, or

15 during their use.

The metals in their pure form generally exhibit poor adhesion characteristics for bonding to polymeric substrates. A multi-layer printed circuit board having copper signal conductors sandwiched between dielectric layers formed from epoxy resins is required to have an interlamine bond strength between the copper film layer and the dielectric layer of at least 7.5 N/cm. If an attempt is made to laminate an untreated copper coated epoxy substrate to an epoxy based substrate, the interlamine bond strength is generally found to be in the range of 1.5 to 3.5 N/cm.

20

First attempts to improve the interlamine bond strength of copper films to epoxy resin based dielectrics involved roughening or texturing the metal surface mechanically. The metal surface was vapour blasted with aqueous slurries of alumina or silica. Recently, it has been the practice to treat the copper film surface prior to lamination with a solution of sodium chlorite (NaClO_2) and sodium hydroxide (NaOH) at temperatures near to boiling to convert the copper (Cu) film surface to more adherent copper oxide (see

25

e.g. **Document I**). This chlorite treatment step generally raises the interlamine bond strength of the copper film layer to the required level.

5 A drawback to the chlorite adhesion promoting treatment, as used in the art, is that the oxide coatings formed are often still not satisfactory. It often results in areas of poor copper to polymer adhesion after lamination.

10 Accordingly, it is the object of this invention to provide an improved process for increasing the adhesion of polymeric layers laminated to metallic surfaces, e.g. to prepare multi-layer articles particularly adapted for the manufacture of printed circuit boards. More particularly, the invention therefore aims at improvements in the preparation of circuit boards which prevent or at least greatly reduce the risk of delamination of the boards during the various processing steps during the production of the circuitry or thereafter during their use in electric or electronic devices.

15 The present invention therefore relates to a process for manufacturing printed circuit boards of at least one dielectric polymeric substrate material and at least one metal layer adhered to at least one surface of the said substrate by the following steps:

- 20 (a) mechanically and chemically pretreating a metal, preferably a copper, foil or layer in such a way that the surface of the metal foil or layer is textured (roughened) and then
- (b) bringing the textured metal surface into contact with at least one surface of the substrate and
- (c) thereby forming an adhesive bond between the surfaces.

25 A metal film having one of its surfaces already bonded to a polymeric substrate is referred to herein as a "layer" whereas a self-supporting film having two free surfaces is referred to as a "foil".

30 This process can be used to laminate a metal foil to a prepreg or to laminate a printed circuit board to a further prepreg in order to prepare multi-layer boards containing internal strip conductors or signal conductors or electric power tracks.

In step (a) the metal film layer or metal foil, usually copper, is treated in accordance with the present invention by impinging onto the film or foil a pressurised stream of a slurry or suspension of metal oxide particles whereby the surface is roughened and the surface area available for bonding increased. Suitable metal oxide particles include particles of aluminium and/or silicon oxide, preferably aluminium oxide particles. The metal oxide slurry generally contains 10 to 30 percent by weight (mass%) of metal oxide solids suspended in a suitable liquid suspending medium. The suspending medium is usually pure water though it may contain viscosity regulators and surfactants provided they do not affect the abrasive properties of the metal oxide particles. The average particle size of the metal oxide particles suspended in the slurry generally will be less than 100 μm . For aluminium oxide particles, the preferred size is from 15 μm to 50 μm . The metal oxide slurry is impinged on the metal film surface by vapour blasting the metal surface with the slurry being emitted from a suitable jet device at a pressure of greater than 0.2 MPa (2 bar) and preferably 0.25 to 0.55 MPa. The vapour blasting should continue for a sufficient time to roughen the surface and this will generally be 0.5 to 5 minutes or more, depending upon the abrasiveness of the particular metal oxide particles used. For aluminium oxide particles, the time is generally from 0.5 to 3 minutes, preferably 1 to 2 minutes.

After the metal surface has been subjected to the pressurised metal oxide slurry treatment, the treated metal layer is rinsed with clean water to remove any surface contamination caused by traces of metal oxide that may remain on the metal surface. After being subjected to the pressurised stream of metal oxide slurry, the metal film layer is exposed to a chemical treatment to further improve the bonding strength of the laminate.

According to one embodiment of the invention, the metal surface is exposed, after the metal oxide treatment, to a plasma containing a gaseous fluorohydrocarbon to further modify the surface. In this additional step of the present invention, the pretreated metal surface is exposed to the plasma generated in a reactor of the known type used for plasma etching. The practice of plasma etching is well known in the art.

In the plasma treatment in accordance with the practice of the present invention, the plasma gas comprises a volatile fluorohydrocarbon of up to two carbon atoms in which most of the substituents on the carbon atoms are fluorine atoms. CF_4 , C_2F_6 , CHF_3 and $\text{C}_2\text{H}_2\text{F}_4$ are examples of suitable fluorohydrocarbons.

The fluorohydrocarbon(s) may be used alone or as a mixture with oxygen and/or an inert gas such as argon or nitrogen. When gaseous mixtures are used for generating the plasma the mixture generally contains, on a volume basis, from 5 to 100% of the fluorohydrocarbon, from 0 to 95% of the inert gas and from 0 to 90% oxygen. Preferably, the gaseous mixture contains 60 to 80 vol.% of the fluorohydrocarbon, and 10 to 30 vol.% oxygen and 20 to 30 vol.% of the inert gas. Carbon tetrafluoride (CF₄) is the fluorohydrocarbon gas preferred for use in the plasma treatment step of the process of the present invention.

Optionally, the exposure of the film layer to the fluorohydrocarbon containing plasma is interrupted after the metal surface has been subjected to the plasma environment containing the fluorohydrocarbon for 10 to 30 minutes, and the fluorohydrocarbon containing gas in the reactor is replaced with a gaseous plasma consisting essentially of oxygen. The treatment of the metal substrate is then continued for an additional 5 to 15 minutes.

The plasma treatment step of the process of the present invention is conveniently conducted at temperatures from room temperature (e.g. 20°C) up to 50°C in a parallel plate reactor of the type conventionally used for plasma etching. In such a reactor, there are one or more pairs of parallel plate electrodes with one electrode in each pair being powered to from 1000 to 5000 watts (radio frequencies, RF) and the other electrode in each pair being grounded. The total gas pressure used is typically below 0.700 hPa (mbar) and the total gas flow is typically 1500 to 4000 cm³/min at standard conditions (0°C, 1013 hPa).

According to a second embodiment, the metal film surface, in particular copper, after the metal oxide treatment, is then exposed to an iodine plasma at pressures and temperatures similar to those in the above embodiment, while the electrical requirements are not necessarily so stringent as above. The electric power may be in the range of 40 to 100 watts (RF). The treatment results in a metal iodide layer being formed. This layer is then conveniently removed by a 10 weight% (= mass%) hydrochloric acid solution which has no damaging effects on the metallic surface or any plastic substrate laminated therewith. The remaining metal surface is then highly textured.

A still further embodiment of the invention can be used when the metal is copper. In this embodiment, the metal oxide treatment of the copper surface, as described above, is followed by a chemical treatment wherein the copper surface is chemically oxidised in accordance with **Document I** with aqueous alkaline

solutions of sodium chlorite to give an oxidised copper surface. Then, this surface is treated with an aqueous solution of a reducing agent having a pH value of 1 to 6 and containing either zinc formaldehyde sulfoxylate ($\text{ZnSO}_2 \cdot \text{CH}_2\text{O} \cdot 2\text{H}_2\text{O}$) or sodium hypophosphite (NaH_2PO_2) or both. The treatment is carried out, in general, at a temperature of from 40 to 90°C using a solution usually containing the
5 reducing agent in an amount of 5 to 30 g/l. When the multi-layer printed circuit board, prepared according to this embodiment, is subjected to subsequent operations, generation of "haloing" can be completely prevented or reduced to a considerable extent.

In each case, the treated surface is thoroughly rinsed after each step and dried prior to the laminating step
10 in order to remove all residues of the treating agents and any loose parts of the surface.

In process step (b) the metal surface is laminated to a dielectric polymeric substrate material. Suitable dielectric substrate materials include mainly thermosetting polymers. Typical thermosetting polymeric materials to which the metal surface may be laminated include epoxy resins, phenolic based materials and
15 polyimides. The dielectric materials may be moulded articles of the polymers. The polymers may contain fillers and/or reinforcing agents, such as glass-fibres. Examples of some phenolic type materials include copolymers of phenol, resorcinol and/or cresol. All these materials have already been used in this field.

The lamination or bonding is conveniently carried out according to the processes already known in the
20 art, e.g. in a pre-heated laminating press. The time of the pressing operation is variable depending upon the particular dielectric substrate material employed and the temperature and pressure employed. One to two hours are, in general, adequate.

A laminate particularly suitable for use in the preparation of a multi-layer printed circuit board according
25 to the process of this invention is prepared, for example, by placing a prepreg sheet made of a **B-stage** (i.e. not fully cured but self-supporting) thermosetting epoxy resin impregnated glass fabric sheet in a laminating press on top of a copper film layer deposited on a fully cured epoxy impregnated glass fabric sheet, the metal layer having been previously treated in accordance with the above described step (a). The

actual bonding and final curing of the **B-stage** prepreg to the treated copper film surface is accomplished by simultaneously pressing the laminating components together and baking at a temperature of 120 to 235°C, preferably at 150 to 200°C, at a pressure of 350 hPa (mbar) to 7 MPa (70 bar) for a period of time ranging from 5 minutes to 120 minutes.

5

The metal film thickness may vary widely although, preferably, it will generally range from 20 µm to 750 µm in thickness. In a like manner, the thickness of the thermosetting resin substrate utilised may vary from 350 µm to 3.5 mm, or more, e.g. by increasing the number of layers of prepreg in the laminating step.

10

The following examples further illustrate the invention, it being understood that the invention is in no way intended to be limited to the details described therein.

Example 1, Comparative Tests C1 to C4

15

Epoxy laminates having a thickness of 250 µm and bearing copper layers of 50 µm were placed in a closed chamber at room temperature and blasted with a pressurised spray of a slurry containing 20% by weight alumina in deionised water pressurised to 0.4 MPa for 1 min 20 s. Then the treated copper surfaces were thoroughly rinsed and dried by pressurised air. The treated copper coated laminates were placed in a parallel electrode plasma reactor between an RF powered electrode and a grounded electrode. The input RF power was 3000 watts and the pressure during etching was about 0.3 hPa. The total gas flow averaged about 2000 cm³/min at standard conditions. Plasma treatment was initially carried out for 20 minutes using a variety of gas mixtures containing CF₄. Then the gas feed and RF power to the reactor were interrupted and the samples allowed to remain in the chamber for 10 minutes. Thereafter the gas feed and RF power to the reactor were resumed but the original CF₄ gas mixture was replaced with O₂ gas and etching continued for an additional 15 minutes. The dried samples were then laminated to an epoxy prepreg by a conventional multi-layer (4 layers) procedure; i.e. at 2.5 MPa and 160°C for 80 minutes.

25

The laminates were subjected to the following standard peel test: The peel value of a 2.5 cm wide strip when pulled at a 90° angle from the substrate at a rate of 2.5 cm/min was measured. The peel values of the laminates in which the copper film surface was prepared in accordance with this Example 1 are summarised in Table 1 below.

30

For purposes of comparison, the procedure of Example 1 was repeated with the exception that at least one of the sequential treatment steps of the process of the present invention was not used. The peel strength values of these comparative laminates, designated by the symbol "C", are also summarised in Table 1 below.

5

Example 2

A double-sided copper-clad glass-fibre reinforced epoxy laminate (thickness of laminate is 0.8 mm and thickness of copper foil is 70 μm) was prepared. About half of the copper layers was removed by a known
10 etching method to provide strip conductors. After having been treated with the metal oxide as described in Example 1, the copper surfaces of the laminate were chemically oxidised with an aqueous solution containing sodium hydroxide (15 g/l), sodium chlorite (31 g/l) and sodium phosphate (Na_3PO_4) (15 g/l) at 90°C for 5 minutes to form black oxidised copper surfaces and washed with water. The resulting
15 oxidised copper surfaces of the laminate were treated with dilute sulphuric acid and then, after rinsing with water, again oxidised at 80°C with a solution of the above components containing an increased amount of sodium hydroxide (25 g/l). After rinsing with water, the surfaces were reduced with an aqueous solution containing zinc formaldehyde sulfoxylate ($\text{ZnSO}_2 \cdot \text{CH}_2\text{O} \cdot 2\text{H}_2\text{O}$) (10 g/l) and acetic acid (10 ml/l) having a pH of 3 to 4 at 80°C for 1.5 minutes and were carefully washed with water and dried at 130°C for 30 minutes to obtain the "internal circuit board".

20

Three sheets of glass-fibre reinforced Epoxy prepreg (resin content of 52% and thickness of 0.1 mm) and copper foil having a thickness of 18 μm were stacked on both sides of the resulting internal circuit board. All layers were laminate-moulded at 175°C and 400 N/cm² (4 MPa) for 2 hours to obtain a multi-layer board, and cooled. A thousand perforations having a diameter of 0.4 mm were made through the resulting
25 4-ply board by a drill at 80,000 rpm at intervals of 2.54 mm.

The board was immersed into a 4 N hydrochloric acid solution for 5 minutes. Generation of "haloing" was evaluated (the maximum breadth of the pink ring around the perforations and the pink area at the outer edge in μm).

30

The results are shown in Table 2.

Example 3

The procedure of Example 2 was repeated except that the zinc formaldehyde sulfoxylate was replaced by sodium hypophosphite (30 g/l NaH_2PO_2). The results are shown in Table 2.

5

Comparative Tests C5 and C6

The procedures of Examples 2 and 3 were repeated except that the resulting oxidized copper surfaces of the laminate were immersed in an alkaline aqueous reducing solution of 10 g/l $\text{ZnSO}_4 \cdot \text{CH}_2\text{O} \cdot 2\text{H}_2\text{O}$ and 5/l g NaOH at 75°C for 15 minutes (C5) or an alkaline aqueous reducing solution containing 30 g/l NaH_2PO_2 and 5 g/l NaOH at 65°C for 10 minutes (C6). The results are shown in Table 2.

Example 4

15 The initial laminate as described in Run 1 of Example 1 and as treated with the metal oxide as described in Example 1 was placed in an evacuated chamber similar to that used in Example 1 for treatment with a cold plasma prepared from iodine (I_2) gas. The pressure in the chamber was 3.5 mPa, the RF power used was 50 watts, reaction time was 5 minutes. The iodised laminate was then removed from the chamber and the copper iodide was removed by treating the laminate with 10% aqueous HCl solution. The surface was
20 highly textured and could be laminated with a further prepreg as described in Example 1. The peel strength was 13.5 N/cm.

Table 1

Run	Pretreatment	Initial Etch Gas Composition (volume %)			Interlaminar Peel Value
No.		Argon	Oxygen	CF_4	(N/cm)
1	Alumina	70	20	10	15.4
C1	None	70	20	10	2.7
2	Alumina	90	0	10	11.6
C2	None	90	0	10	2.1
C3	Alumina	100	0	0	5.5
C4	None	100	0	0	0

Table 2

	Reducing solution		"Haloing" (maximum width in μm)	Interlaminar Peel Value (N/cm)
	Reducing agent	(pH)	4 N HCl	
Ex.2	$\text{ZnSO}_4 \cdot \text{CH}_2\text{O} \cdot 2\text{H}_2\text{O}$	3 - 4	0	16.6
Ex.3	NaH_2PO_2	3 - 4	0	16.2
C5	$\text{ZnSO}_4 \cdot \text{CH}_2\text{O} \cdot 2\text{H}_2\text{O}$	>8	100	11.0
C6	NaH_2PO_2	>8	150	10.3

CLAIMS

1. A process for manufacturing printed circuit boards of at least one dielectric substrate material and at least one metal layer adhered to at least one surface of the said substrate by the following steps:
 - (a) mechanically and/or chemically pretreating a metal foil or layer in such a way that the surface of the metal foil or layer is roughened and then
 - (b) bringing the rough metal surface of at least one metal foil or layer into contact with at least one surface of the substrate and
 - (c) thereby forming an adhesive bond between the said surfaces.
2. Process according to claim 1 characterised in that the dielectric substrate is a prepreg of a thermosetting resin which is finally cured in step (c).
3. Process according to claim 1 characterised in that the metal is copper.
4. Process according to any one of the preceding claims characterised in that the metal foil or layer is pretreated by impinging on its surface(s) a stream of a slurry of fine metal oxide particles under high velocity and then further etching the surfaces by chemical treatment.

COMMUNICATION

1. While according to page 3 of your description the process claimed includes both mechanical and chemical treatment of the metal in step (a), claim 1 requires only one of these treatments. This renders the application as a whole unclear (Art. 84 EPC).
2. Moreover, in view of this wording of claim 1, claims 1 to 3 appear to be anticipated by **Document I**. On page 2 of the application, reference is made to the fact that mechanical treatment of the metal layer is well known in the art as well.
3. **Document II** appears to be even closer to the subject-matter claimed in your application. This document discloses a process wherein metal layers are bonded to dielectric polymer substrates after having been mechanically and chemically treated. In particular, the two runs in the example of this document appear to correspond directly to the present Example 1 (the differences in the peel values obviously fall within normal tolerances). Hence, the example of **Document II** taken by itself demonstrates that the process claimed in claims 1 to 4 does not comply with Art. 52 (1) and 54 (1) and (2) EPC.
4. **Document III** relates to another process for preparing similar circuit boards wherein - optionally after "sand blasting" with hard material such as alumina - the copper surface is modified by means of an iodine plasma to enhance the bonding strength of the copper to a polymer substrate. Particular reference is made to claim 3 of the document. This document also constitutes an anticipation of your claims 1 to 4.
5. The percentages of the components of the fluorohydrocarbon plasma on page 5 of the description do not sum up to 100 % in each case. This fact should be taken into account if preparing claims which relate to this composition.
6. If you wish to continue with the application, you are invited to submit claims which take the aforementioned objections into account and comply with the requirements of the EPC, especially

with regard to novelty, inventive step, clarity, disclosure in the application documents as originally filed and, if necessary, unity (Art. 54(1) and (2), 56, 84, 123(2) and 82 EPC).

7. In your reply, you should also identify the difference between the new claims and the state of the art and its significance, and present the invention in such a way that both the technical problem to be solved vis-à-vis the state of the art and the solution found (see Rule 27(1)(c) EPC and Guidelines C-IV, 9.5), as well as your position on the question of inventive step, can be understood.
8. According to the Guidelines (C-III, 4.4) an independent claim should specify clearly all the essential features needed to define the invention, i.e. each independent claim must indicate all the features necessary to solve the problem on which the invention is based.
9. Your attention is drawn to the fact that the application may not be amended in such a way that its subject-matter extends beyond the content of the application as filed (Art. 123(2) EPC). Therefore, and also in view of the Guidelines E-II, 1 and C-VI, 5.4, you should explain from where in the original application documents the new features in any newly formulated claims have been directly and unambiguously derived.

DOCUMENT I (State of the Art)

The present invention relates to a method of manufacturing a multi-layer printed circuit board comprising a plurality of printed circuit layers with adhesive insulating layers interposed between them. The method is effective in preventing defective adhesion between a printed circuit layer and the adhesive insulating layer, and in preventing treatment agents which are used in the manufacturing process from remaining at
5 an interface between the printed circuit layer and the adhesive insulating layer.

10

In order to overcome this problem, it has been proposed to texture the surface of the printed circuit layer formed of a copper foil or layer by oxidising the surface thereof by using an aqueous alkaline solution of sodium chlorite, thereby forming an oxide film consisting of CuO and Cu₂O.

15

The oxide film, which is resistive to an alkaline solution, is relatively easily dissolved by an acidic solution, when its surface is exposed to an acidic treatment agent in the further processing of the multi-layer printed circuit board. As a result, a phenomenon of so-called "haloing" occurs, in particular in the form of pink rings at perforations drilled into the board to mount electronic components.

20

Haloing causes deterioration of the bonding strength at those parts of the interface between the different layers which came into contact with acidic solutions, and raises the problem of peeling (delamination) in the long term. Moreover, the reliability of the electric contacts on the multi-layer printed circuit board is reduced.

25

It has been found that CuO in the oxide film formed in accordance with the conventional method is not sufficiently resistant against acids used in the further processing of the boards since it is easily dissolved.

Accordingly, the object of the present invention is to provide a method of manufacturing a multi-layer
printed circuit board, which enables the extent of the haloing to be controlled to 100 µm or less and to

improve the bond strength at the interfaces between copper layers and insulating (dielectric) layers in printed circuit boards.

According to the present invention, there is provided a method of manufacturing a multi-layer printed circuit board from individual boards which bear a printed copper circuit on a dielectric polymeric support, the process comprising the steps of (a) oxidising the copper circuit with a first alkaline oxidising solution, (b) etching the first oxidised circuit thus obtained with a diluted acidic solution thereby removing at least part of the CuO contained in the surface of this layer, (c) oxidising the said first oxidised and etched circuit with a second alkaline oxidising solution having a higher alkalinity, and (d) laminating a plurality of said oxidised boards with an insulating layer interposed therebetween.

As in the past, sodium chlorite can be used as an oxidising agent. It is dissolved in water, and sodium hydroxide is added to obtain the required alkaline oxidising solutions. The second alkaline oxidising solution is higher in alkalinity than that of the first alkaline oxidising solution.

15

Step (a) corresponds to the conventional process and results a CuO/Cu₂O-film on said copper circuit. In step (b) CuO contained in the oxidised layer is dissolved and removed. Thereafter in (c), the oxidized layer is subjected to a second oxidising treatment by using a second alkaline oxidizing solution. As a result, the finally obtained oxidised layer is Cu₂O-enriched, containing 80% or more of Cu₂O with respect to the total content of copper oxide in the layer. In step (c) the treatment temperature is maintained in the range of 40 to 85°C, which is lower than the conventional treatment temperature of 90 to 95°C.

20

The laminating step and subsequent steps in the further processing of the circuit board can be carried out in the conventional manner.

25

The above steps (a), (b) and (c) carried out before step (d) result in an increased quality of the multi-layer

printed circuit board due to the effective inhibition of the haloing phenomenon.

Example

- 5 (1) A glass fibre-reinforced epoxy plate laminated on both surfaces to copper foils was photo-etched in the conventional manner to obtain a printed circuit board. (2) The printed circuit board was oxidised with a solution containing 17 g/l of Na_3PO_4 , 21 g/l of NaOH and 43 g/l of NaClO_2 at 90°C for 4.5 minutes and the product was washed with water. (3) Then, the printed circuit board was further treated with a 10% sulphuric acid solution to dissolve the CuO contained in the layer and washed with water again.
- 10 (4) The etched oxidized film was then subjected to a second oxidising treatment for three minutes at 80°C using a solution containing the same ingredients as the first alkaline oxidising solution, except for the amount of NaOH which was increased to 31 g/l. The board was washed again with cold and thereafter with hot water. Finally, the circuit board was dried at a temperature of 130°C.
- 15 A number of printed circuit boards obtained in this way were compressed with heating to obtain a laminated multi-layer printed circuit board.

Perforations (diameter 0.35 mm) were drilled into the multi-layer printed circuit board. The board was further processed in a conventional manner. Finally, the breadth of the haloing formed on the multi-layer

20 printed circuit board was found to reach a maximum of 64 μm .

DOCUMENT II (State of the Art)

In many applications, strong adherence between a metallic surface and a polymeric surface is essential. Thus, the strong adherence of metal to polymer is critical in the manufacture of multi-layer printed circuit boards in the electronics, telecommunications, computer and other industries.

5 In the manufacture of electronic devices, such as computers, printed circuit boards are widely used to support discrete electronic components and to provide the electrical circuitry between the components. The printed circuit boards of today are composite structures having a central core, typically a dielectric material such as glass fibre reinforced thermosetting resin such as an epoxy resin, phenolic polyester resin or other thermosetting resin, referred to in the art as a "prepreg". The prepreg has applied on either side
10 thereof metallic circuitry, usually formed of a metal film layer such as copper. The metal film layer is etched or otherwise processed according to the art to provide circuits of predetermined geometrical configuration. The printed circuit board may be a two-sided composite board having circuitry on both sides of the dielectric layer, or it may be a laminated multi-layer board which also contains internal layers of signal conductors and power tracks separated by the dielectric layer. The laminated multi-layer printed
15 circuit boards are prepared from individual composite circuit boards which are laminated to form the multi-layer structure having an etched metal circuitry sandwiched between the prepreg layers. The laminated multi-layer boards are provided with perforations which allow for the interconnection of the various circuit conductors on the different metal layers. Discrete electronic components (resistors, capacitors, semiconductors such as transistors, integrated circuits, diodes, and the like) are mounted on
20 the printed circuit board and electrically connected to the strip conductors, signal conductors or power tracks of the circuit board.

Various methods have been used to provide a metal film layer on one or both sides of a prepreg substrate. When such metallised substrates are further laminated to polymeric prepreg substrates to form a multi-
25 layer printed circuit board, the adhesion of the metal layers to these further substrates is often inadequate, especially with respect to polymer prepregs based e.g. on epoxy resins. Metals in their pure form generally

exhibit poor adhesion characteristics for bonding to polymeric substrates. For example, the interlaminar bond strength between a copper film layer and a dielectric support layer should be at least about 7.5 N/cm in a multi-layer board. The interlaminar bond strength of untreated copper to an epoxy based substrate is, in general, in the range of up to 3 or 4 N/cm.

5

To improve the interlaminar bond strength of copper films to epoxy resin based dielectrics, it has been the practice to treat the copper film surface prior to lamination with a solution of sodium chlorite and sodium hydroxide at temperatures near boiling to convert the copper film surface to a more adherent copper oxide. This chlorite treatment step generally raises the interlaminar bond strength of the copper
10 film layer to the required level. A drawback to the chlorite adhesion promoting treatment, as used in the art, is that the oxide coatings formed are still not satisfactory. It often results in areas of poor copper to polymer adhesion after lamination.

Accordingly, it is a principal object of this invention to provide an improved process for enhancing the
15 adhesion of polymeric layers laminated to metallic surfaces, e.g. to prepare multi-layer articles particularly adapted for the manufacture of printed circuit boards. This treatment aims at the preparation of printed circuit boards with much less risk of delamination during their manufacture or thereafter in service.

The object is achieved by a method for promoting the adhesion of polymeric materials to metal surfaces
20 which comprises sequentially impinging on the surface of the metal a stream of a slurry or suspension of hard metal oxide particles which texture the surface. Then the treated metal surface is exposed to a plasma containing a volatile fluorohydrocarbon to further modify the metal surface.

The inventive method improves the adhesion of copper circuit conductors in the internal layers of a multi-
25 layer printed circuit board to dielectric substrates.

As will hereinafter be further demonstrated by using a combination of metal oxide and fluorohydrocarbon plasma treatment steps, the interlaminar bond strength values of a metal film layer, such as copper, to

a polymeric surface, such as an epoxy polymer, are found to be in excess of 8 N/cm.

The metal surface treated according to the present invention may be any metal to which a polymer may adhere. In the electronics industry this generally will be copper, aluminum or silver. Copper films
5 deposited on epoxy dielectric surfaces which can be laminated to epoxy based prepregs in order to prepare printed circuit boards are generally prepared by known techniques, e.g. electroless or vacuum metallisation.

The metal film layer or metal foil is treated by impinging onto the film or foil a pressurised stream of a
10 slurry or suspension of metal oxide particles. The surface is thereby roughened by increasing the surface area available for bonding. Suitable metal oxide particles include oxides of aluminium, silicon and/or titanium. Preferably aluminium oxide particles are used. The metal oxide slurry generally contains about 10 to about 30 wt.% and preferably about 15 to about 25 wt.% of metal oxide solids suspended in a suitable liquid suspending medium, e.g. water. The suspending medium may contain surfactants and
15 viscosity regulators provided they do not affect the abrasive qualities of the metal oxide particles. The average particle size of the metal oxide particles, in particular that of alumina, will generally be from about 15 μm to about 70 μm , in particular about 35 μm . The metal oxide slurry is impinged on the metal film surface by vapour blasting the metal surface with the slurry being emitted from a suitable jet device at a pressure of preferably about 2.5 to about 5.5 bar. To roughen the surface about 0.5 to 5 minutes will in
20 general be sufficient depending on the particles used. For alumina, about 1 to 2 minutes may be sufficient.

After the metal surface has been subjected to the above treatment, the metal layer is thoroughly rinsed with water to remove any surface contamination. After drying, the metal film layer is further modified by exposing it to a plasma of a gaseous fluorohydrocarbon generated in a reactor of the type used for plasma
25 etching for about 10 to about 30 minutes. The practice of plasma etching is well known in the art.

The plasma comprises a volatile fluorohydrocarbon having one or two carbon atoms such as CF_4 , C_2F_6 , CHF_3 , and $\text{C}_2\text{H}_2\text{F}_4$. These compounds may be used alone or as a mixture with oxygen and/or an inert gas

such as argon or nitrogen. When gaseous mixtures are used, they preferably contain about 60 to about 70 vol.% fluorohydrocarbon, about 10 to about 20 vol.% oxygen and about 20 to about 30 vol.% inert gas. Thereafter, the fluorohydrocarbon containing plasma in the reactor may be replaced with a gaseous plasma consisting essentially of oxygen for an additional period of 5 to 15 minutes.

5

In the parallel plate reactor of the type conventionally used for plasma etching having one or more pairs of parallel plate electrodes, one electrode in each pair is powered to from about 1000 to 5000 watts (RF) and the other electrode in each pair is grounded. The total gas pressure used is typically about 0.100 to 0.700 mbar and the total gas flow is typically about 1.5 to 4 litres/min at standard conditions (0°C,

10 1013 mbar). The reaction temperature will be held at about 20 to 50°C.

Finally, the metal surface treated as described above can be laminated to a dielectric polymeric material, in particular, a thermosetting polymer. Epoxy resins, phenolic based materials and polyimides may be used. They may or may not be moulded and they may contain fillers and/or reinforcing agents such as

15 glass-fibres. Examples of suitable materials include copolymers of phenol, resorcinol and/or cresol.

Laminating is conveniently carried out as generally known in the art, e.g. in a pre-heated laminating press. Mostly, about 1 to 2 hours are adequate for the pressing operation.

20 Lamination can, for example, be carried out by placing a prepreg sheet comprising a **B-stage** (ie. not fully cured but self-supporting) thermosetting epoxy resin impregnated glass fabric sheet in a laminating press on top of a copper film layer deposited on a fully cured epoxy impregnated glass fabric sheet, the copper layer having been previously treated as described herein above. The laminate is prepared and cured by simultaneously pressing the components together and baking them at a temperature of about 150°C to

25 200°C at a pressure of about 350 mbar to 70 bar for about 5 to 120 minutes.

The metal film thickness may vary widely although, preferably, it will generally range from about 20 µm to about 700 µm in thickness. The thickness of the thermosetting resin substrate utilised may vary from about 350 µm to 3.5 mm, or more, according to the number of layers of prepreg in the laminating step.

30

Example

250 μm thick epoxy laminates bearing copper layers of 50 μm were placed in a closed chamber at ambient temperature and blasted with a pressurised spray of a slurry containing 20% by weight alumina in deionised water pressurised to 4 bar for about 80 s. Then the treated copper surfaces were thoroughly rinsed and dried by pressurised air. The treated copper coated laminates were placed in a parallel electrode plasma reactor between an RF powered electrode and a grounded electrode. The input RF power was 3000 watts and the pressure during etching was about 0.3 mbar. The total gas flow averaged about 2 litres/min at standard conditions. Plasma treatment was initially carried out for 20 minutes using a variety of gas mixtures containing CF_4 . Then the gas feed and RF power to the reactor were interrupted and the samples allowed to remain in the chamber for 10 minutes. Thereafter, the gas feed and RF power to the reactor were resumed but the original CF_4 gas mixture was replaced with O_2 gas and etching continued for an additional quarter of an hour. The dried samples were then laminated to an epoxy prepreg by a conventional multi-layer (4 layers) procedure; i.e. at 25 bar and 160°C for 1 hour and 20 minutes.

The so-prepared laminates were subjected to the following standard peel test: The peel value (in N/cm) of a 2.5 cm wide strip was measured when pulled at a 90° angle from the substrate at a rate of 2.5 cm/min. The peel values of the laminates in which the copper film surface was prepared in accordance with this Example are summarised in the Table.

Table

Run	Initial Etch Gas Composition (volume %)			Peel Value
No.	Argon	Oxygen	CF_4	N/cm
1	70	20	10	15.5
2	90	0	10	11.7

DOCUMENT III (State of the Art)

The invention relates to a room-temperature process for texturing copper to improve adhesion of coatings to the copper surface through mechanical as well as chemical bonding. The copper can be part of a copper-plastic laminate.

- 5 Copper (and even more silver) surfaces have, in general, insufficient adhesion to additional material due to the smoothness of the metal surfaces, as well as their low chemical reactivity. If these metals are to be laminated with a plastics material, mechanical as well as chemical bonding should be provided wherever possible.
- 10 Abrasive techniques are known for increasing the surface area and providing a mechanical bond of copper to plastics. Wet etching techniques to modify the surface of copper for increasing the surface area for mechanical bonding are also known. They are however susceptible to trouble and subject to contamination from the etching bath.
- 15 Purely chemical treatments of plastics, so as to achieve an interface layer which sticks to the plastics and to which succeeding layers will adhere have been described. This type of approach is impractical in situations where a pattern of copper is to be covered with a layer of plastics in a plastics-copper-plastics sandwich, because of electrical short circuit problems as well as plastics-plastics and plastic-copper adhesion problems.

20

The present invention is a room-temperature process for texturing metal with an iodine plasma. This treatment improves adhesion of coatings to the metal surface through mechanical as well as chemical bonding. In order to start from a clean metallic surface, it is sometimes advantageous to pretreat the metal surface by "sandblasting" with an aqueous slurry of hard inert material such as alumina or silica. The

- 25 invention will now be described in more detail with respect to the treatment of copper surfaces.

An iodine plasma is produced by feeding iodine gas under low pressure into a reaction chamber and applying an RF potential as known in the art. Unprotected surface areas of the copper form copper iodide.

When the copper iodide is conveniently removed by a 10% hydrochloric acid solution, the remaining surface is highly textured. This treatment can be carried out in a way that no surfaces laminated with the copper are damaged.

- 5 The invention provides a process for texturing metal surfaces to improve adhesion to plastics, as defined in the claims. More particularly, a copper iodide surface is created on metallic copper and then removed to leave a clean, textured copper surface to which plastics will bond readily.

The copper may be in the form of a layer or patterns already bonded to the final substrate or may be
10 copper on a temporary substrate from which it may be transferred to a final substrate.

The copper is placed in an evacuated chamber, or arrangements are made for passing the copper through the evacuated chamber for iodization. An iodine plasma is produced as described above. In general, the process takes about 5 minutes. The copper iodide which is formed is then removed by washing with a
15 10 % HCl solution. After the copper iodide removal, the remaining surface is highly textured.

Operating parameter chart

	pressure in the vacuum chamber	3 to $4 \cdot 10^{-3}$ Pa
20	Substrate temperature	Room Temperature (20 °C)
	I ₂ Source Temperature	30 °C
	Power	50 Watts

This process provides a simple method for improving adhesion of copper surfaces to plastics. Peel values
25 of 9 to 10 N/cm can be achieved. Copper patterns already adhering on plastics (or cemented to plastics) may be textured in a continuous or semi-continuous batch mode limited by vacuum chamber characteristics. Copper thickness is not critical, nor is plastics thickness.

Plastics of a wide variety may be used including polyimide as well as a host of other plastics, such as

epoxy resin preregs which may be fully cured in contact with the copper surface.

Claims

1. A process for providing a textured surface of improved adhesion susceptibility on a copper sample characterised by placing the sample within a chamber containing iodine vapour at a pressure of 3 to 4 mPa; and while the sample is between room temperature and 50°C, applying an RF irradiation of approximately 50 watts; and removing the copper iodide formed from the sample.
2. The process according to Claim 1 in which the copper iodide is removed by washing the sample in a dilute acid solution, preferably a solution of about 10% HCl.
3. The process of Claim 1 in which the copper sample comprises a copper-plastics laminate and said plastics is polyimide or an epoxy prepreg.