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PATENT SPECIFICATION

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(54) METALLIZING INSULATING SUBSTRATES

(71) We, PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED of Abacus House, 33 Gutter Lane, London, E.C.2., a British Company, 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:—

The invention relates to a method of metallizing a synthetic plastics material either uniformly or according to a pattern, and in particular to an additive method of photographically manufacturing electrically conductive metal patterns on an insulating substrate consisting of a synthetic resin, specifically printed circuits and the products obtained by the use thereof.

The term "additive method of manufacturing printed circuits" is used herein to denote a method of the type in which the metal pattern is directly built up on the non-coated layer of the synthetic resin. A method of this type is distinguished from a subtractive method which starts with a layer consisting of a synthetic resin which is coated with a layer of metal the superfluous part of which is removed by etching after the metal parts which comprise the pattern have been coated with a resist.

United Kingdom patent specification No. 1,229,935 describes a method of manufacturing an electrically conductive metal pattern on an electrically insulating layer which itself serves as a support for the pattern or is adhesively secured to a substrate the method including the steps of exposing a photosensitive layer to light in accordance with the desired pattern so as to form a light-reaction product, treating the photosensitive layer prior to or after exposure to light with a solution which contains a salt of copper and/or of Hg, Pd, Pt, Ag or Au so as to form an image consisting of metal nuclei, then intensifying the image optionally using a stabilized physical developer, or after formation of the nuclear metal image has been completed using an electroless copper or nickel or cobalt-plating solution, wherein the photosensitive layer is self-supporting or is provided as a coating on a substrate and consists of a substantially hydrophobic electrically insulating synthetic resin in which or on which finely divided particles of a photosensitive semiconducting oxide are homogeneously distributed, wherein the photosensitive semiconducting oxide forms a light-reaction product which is capable of depositing copper and/or Hg, Pd, Pt, Ag or Au from the solution containing the salt of copper and/or Hg, Pd, Pt, Ag or Au wherein the concentration of the salt in the salt-containing solution is adjusted to a value within a range in which metal of the relevant metal nuclei is deposited, and if necessary the metal salt in the areas of the layer outside the nuclear image are removed before intensification of the image with the electroless plating solution.

In order to obtain good mechanical strength of the photosensitive insulating layer it obviously is necessary for each individual particle of the semiconductive metal oxide to be entirely enveloped by the hydrophobic binder, and this is also desirable to impart the required electric properties to the photosensitive insulating layer. However, this means that at the surface of the photosensitive insulating layer the metal oxide particles are substantially entirely screened from the solution of the metal salt which by reacting with the light-activated particles is to yield the nucleus metal, and also from the intensifying solutions. This means that the formation of metal nuclei and the intensification of the image of metal nuclei on the photosensitive insulating layer are greatly inhibited.

In the cases where the photosensitive insulating layer is coated on a possible insulating base layer, the screening of the semiconductive metal oxide particles available at the surface may be eliminated in a manner described in United Kingdom patent

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specification 1,338,435. According to this specification a partially hardened layer of a binder which consists of thermosetting constituents in which rubber-like constituents are evenly distributed and in which the photosensitive semiconductive metal oxide is dispersed, is subjected to controlled superficial attack by a chemical roughening liquid so that a thickness between about 0.1 μm and 1 μm is etched from the layer.

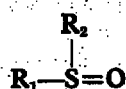
When the photosensitive insulating layer is self-supporting, the said method has the disadvantage that binder layers are used which are only partly hardened, so that the layers have too small mechanical rigidity and too low strength. It is true that thermal hardening performed after the provision of the conducting patterns improves the mechanical properties, but, it also brings about unacceptable changes in the relative positions of the patterns.

United States Patent Specification No. 3,698,940 describes a method of treating a moulded polymerized resin substrate to improve adhesion between the substrate and a metal deposit electrolessly plated thereon. This improved adhesion is achieved by contacting the surface of the substrate with a representative of a given group of dipolar aprotic organic solvents and subsequently with an aqueous chromic acid solution. After catalyzing the surface by means of an aqueous solution of a noble metal salt the catalyzed substrate is heated to a temperature above ambient temperature but considerably below the charring temperature.

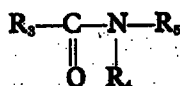
The main disadvantage of this method is that it is much more laborious than the method which starts with a photosensitive insulating layer. Another important disadvantage is that good adhesion is obtained only with substrates of slightly heterogeneous composition, because the combined surface treatment is required to produce anchoring areas for the metal to be deposited.

The invention provides a method of metallizing uniformly or in accordance with a desired pattern an electrically insulating polymerized synthetic resin substrate which is self-supporting or is secured to a support, wherein the substrate contains homogeneously dispersed finely-divided particles of a photosensitive semiconductive metal oxide forming a light-reaction product which is capable of depositing copper and/or Hg, Pd, Pt, Ag or Au from an aqueous solution of the respective metal salt, the method comprising the steps of successively contacting the substrate with a dipolar aprotic solvent (as hereinafter defined) capable of swelling the polymerized synthetic resin and with a chemical roughening agent, exposing the substrate to light uniformly or in accordance with the desired pattern, contacting the substrate before and/or after exposure to light with an aqueous solution of a salt of copper and/or Hg, Pt, Pd, Ag or Au so as to form nuclei of the relevant metal, intensifying the metal nuclei by contacting the nuclei with a stabilised physical developer so as to form an electrically conductive uniform or patterned layer. The electrically conductive layer may be thickened, for example by electrodeposition.

The term "dipolar aprotic solvent" is understood throughout this specification to mean a material being defined by composition I, II or III, wherein composition I has the formula

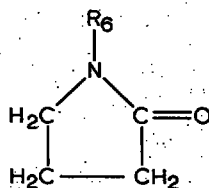


wherein R_1 is a hydrogen atom or an alkyl group containing from 1 to 5 carbon atoms, and R_2 is an alkyl group containing from 1 to 5 carbon atoms, wherein composition II has the formula



wherein R_3 is a hydrogen atom or an alkyl group containing from 1 to 3 carbon atoms, R_4 is a hydrogen atom or an alkyl group containing from 1 to 5 carbon atoms, and R_5

is a hydrogen atom or an alkyl group containing from 1 to 5 carbon atoms, and composition III has the formula



wherein R_6 is an alkyl group having from 1 to 5 carbon atoms.

The method according to the invention which is a combination of the features described in United Kingdom patent specification No. 1,229,935 and 1,338,435 and that described in United States patent specification No. 3,698,940, has the advantage that it is a considerably less laborious method of manufacturing printed circuits than is the latter method.

Another important advantage, however, is that with respect to the choice of the substrate material in which the finely divided semiconductive metal oxide is dispersed there now are many possibilities apart from epoxy-based or phenol-based resins reinforced with glass cloth to which the known method is restricted in practice, for the introduction of the photosensitive semiconductive metal oxide into the substrate material provides a heterogeneous substrate material which when it has been chemically roughened affords excellent anchorages for the metal to be deposited. Thus the slightly heterogeneous composition of the binder combination as required in the known method can be dispensed with owing to the presence of the photosensitive semiconductive metal oxide. Consequently, printed circuits made using the said substrates have very good adhesion between the conductive tracks and the substrate material.

When using the method according to the invention for manufacturing printed circuits the operations of plating through-holes can be fitted in simply. Starting with a base material in which the photosensitive semiconductive metal oxide is thoroughly dispersed, the walls of the holes may be sensitized by exposure to light of the metal oxide uncovered by the hole-drilling operation and by subsequent contacting with a solution of a copper salt or a salt of Hg, Pd, Pt, Ag or Au. The resulting layer consisting of nuclei of the relevant metal can then be intensified by means of a stabilized physical developer or an electroless metal plating bath.

The method may alternatively start with a base material which contains the photosensitive semiconductive metal oxide in the upper layers of both major surfaces, said surface layers furthermore containing a substance which is dispersed in the substrate material and is capable of forming precious metal nuclei when contacted with an aqueous solution of a precious metal salt without exposure to light. In the aforementioned United Kingdom patent specification 1,338,435 such substances are mentioned, such as reducing agents for noble metal ions, redox polymers and ion exchangers charged with reducing ions.

In a preferred embodiment the base material contains an uncharged anion exchanger, within the surface layers which contain the semiconductive metal oxide, whilst after the holes have been drilled activation is effected by means of Pd halides and preferably by means of Pd chloride. This is due to the fact that the activation solution contains mainly $PdCl_4$ ions.

Suitable base materials in which the semiconductive metal oxide is dispersed include, in addition to epoxy resin reinforced with glass fibres, phenol-formaldehyde resin reinforced with paper, and polysulphone foil. Each material has its specific preferred swelling agents. For example, phenol-formaldehyde resin reinforced with paper can be treated successfully with *N*-metal pyrrolidone or dimethyl formamide, epoxy material with dimethyl formamide or *N*-methyl pyrrolidone, polyimide with dimethylacetamide and polysulphone with tetrachloroethane.

Some embodiments of the invention will now be described with reference to the following Examples.

EXAMPLE 1

Sheets of paper are dipped in a bath consisting of a dispersion of TiO_2 in a phenol formaldehyde resin. The dispersion contains 35 g of TiO_2 , to 32 g of phenol and 36 g of formalin. The sheets are pressed with a pressure of 60 kg/cm² at a temperature of 150°C. A TiO_2 -filled phenol-formaldehyde resin reinforced with paper is obtained.

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This substrate material is treated with *N*-methyl pyrrolidone for 3 minutes and is then rinsed in methyl ethyl ketone/methanol (1:1).

The surface is roughened by treating the material for from 8 to 16 minutes in a mixture of

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100 ml of H_2SO_4
100 ml of H_2O
50 ml of H_3PO_4
30 g of sodium bichromate

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at a temperature of 50°C.

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The material is then rinsed in flowing water and neutralized in a 0.1N solution of NaOH. Any TiO_2 particles which may be loosely attached are removed by ultrasonic vibration in water.

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The material is then treated with a solution containing per litre

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1 g of $PdCl_2$
5 ml of HCl (37%)
4 g of Lissapol N
10 g of glycerine

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(Lissapol (Trade Mark) N is a non-ionogenic wetting agent consisting of a condensation product of ethylene oxide with alkyl phenols).

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Subsequently the material is dried and exposed behind a negative by means of a 125 W high-pressure mercury-vapour lamp at a distance of 30 cm for 30 seconds. A latent image consisting of Pd-nuclei is produced at the exposed areas.

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At the non-exposed areas the Pd^{++} ions are removed by rinsing with water.

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The latent image is intensified for 2 minutes in a chemical copper-plating bath at a temperature of 25°C and containing per litre:

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0.14 mol of $CuSO_4 \cdot 5H_2O$
0.30 mol of tetrasodium salt of ethylenediamine-tetra-acetic acid
0.65 mol of NaOH
2.0 mol of formaldehyde.

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The conductive pattern is then intensified to an overall thickness of 25 μm by electrodepositing copper. After a temperature treatment at 170°C for 30 minutes, the adhesion between the metal pattern and the substrate material is 65 g/mm.

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EXAMPLE 2

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TiO_2 is dispersed in an epoxy resin, in an amount of 50 g of TiO_2 per 100 g of resin by grinding the mixture in a ball mill for 24 hours. Glass cloth is impregnated with the pigmented resin and pressed at a temperature of 170°C and a pressure of 35 kg/cm².

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This substrate material is treated with dimethyl formamide for 3 minutes and rinsed in methyl ethyl ketone. It is then chemically roughened, nucleated, imagewise exposed, chemically copper-plated and finally copper-electroplated in a similar manner to that described in Example 1. After a temperature treatment at 170°C for 30 minutes the adhesion between the metal pattern and the substrate material is 160 g/mm.

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EXAMPLE 3

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A homogeneous dispersion of TiO_2 is obtained by grinding finely dispersed particles of TiO_2 together with a polyamide acid (Pyre ML from Du Pont) and *N*-methyl pyrrolidone in the following quantities

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34 g of TiO_2 (A10 of Tiofine)
200 g of polyamide acid
30 g of *N*-methyl pyrrolidone.

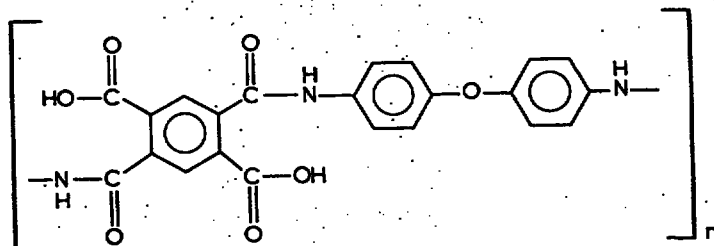
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This dispersion is applied to a support consisting of polyimide (Kapton (Trade Mark) from Du Pont). The adhesive layer is dried at 350°C for 1 hour. The photosensitive adhesive layer then is from 12 to 15 μm thick.

This substrate material is treated with dimethyl acetamide for 1 minute and is then rinsed with a methyl ethyl ketone/methanol (1:1) mixture for 2 minutes. Then the surface is roughened by a treatment in a mixture consisting of:

1% by weight of CrO_3
84% by weight of H_2SO_4
15% by weight of H_2O

at a temperature of 50°C for 1 min. Subsequently the surface is nucleated, imagewise exposed, chemically copper-plated and copper-plated by electrodeposition, similarly to Example 1. After a temperature treatment at 230°C for 30 minutes the adhesion of the copper pattern to the substrate material is 120 g/mm. Polyamide acids have the following structure:



see for example United States patent specifications Nos. 3,179,614; 3,179,631; 3,179,633 and 3,179,634.

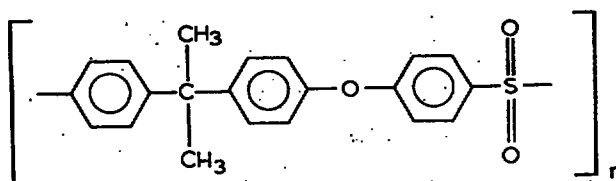
EXAMPLE 4

A support consisting of a polyimide film (Kapton (Trade Mark) from Du Pont) is coated with a layer having a thickness of $15\ \mu\text{m}$ and consisting of a mixture of polysulphone (from Union Carbide) and TiO_2 using the following suspension:

10 g of TiO_2 (Degussa P 25)
60 g of polysulphone (15% solution).
100 g of trichloroethane.

This is obtained by applying a dispersion of TiO_2 in polysulphone and heating it at a temperature of 200°C for 30 minutes. The resulting substrate is treated with tetrachloroethane for 3 minutes and is then rinsed with methyl ethyl ketone/methanol (1:1). The substrate surface is then roughened in a saturated chromic acid solution for 4 minutes. The further treatment is similar to that described in Example 1. After a temperature treatment at 230°C for 30 minutes, the adhesion between the copper pattern and the substrate material is 60 g/mm.

Polysulphones have approximately the following structure:



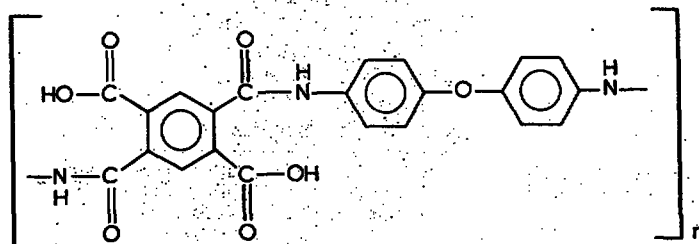
WHAT WE CLAIM IS:—

1. A method of metallizing uniformly or in accordance with a desired pattern an electrically insulating polymerized synthetic resin substrate which is self-supporting or is secured to a support, wherein the substrate contains homogeneously dispersed finely-divided particles of a photosensitive semiconductive metal oxide forming a light-reaction product which is capable of depositing copper and/or Hg, Pd, Pt, Ag or Au from an aqueous solution of the respective metal salt, the method comprising the steps of successively contacting the substrate with a dipolar aprotic solvent (as hereinbefore defined) capable of swelling the polymerized synthetic resin and with a chemical roughening agent, exposing the substrate to light uniformly or in accordance with the desired pattern, contacting the substrate before and/or after exposure to light with an

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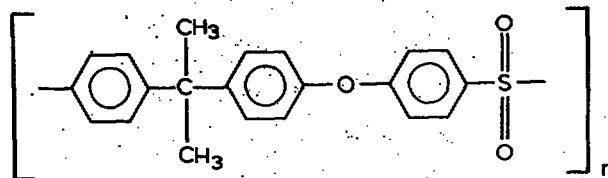
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Polysulphones have approximately the following structure:



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1. A method of metallizing uniformly or in accordance with a desired pattern an electrically insulating polymerized synthetic resin substrate which is self-supporting or is secured to a support, wherein the substrate contains homogeneously dispersed finely-divided particles of a photosensitive semiconductive metal oxide forming a light-reaction product which is capable of depositing copper and/or Hg, Pd, Pt, Ag or Au from an aqueous solution of the respective metal salt, the method comprising the steps of successively contacting the substrate with a dipolar aprotic solvent (as hereinbefore defined) capable of swelling the polymerized synthetic resin and with a chemical roughening agent, exposing the substrate to light uniformly or in accordance with the desired pattern, contacting the substrate before and/or after exposure to light with an



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aqueous solution of a salt of copper and/or Hg, Pd, Pt, Ag or Au so as to form nuclei of the relevant metal, intensifying the metal nuclei by contacting the nuclei with a stabilised physical developer so to form an electrically conductive uniform or patterned layer.

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2. A method as claimed in Claim 1, wherein the electrically conductive uniform or patterned layer is thickened by electrodeposition.

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3. A method of metallizing uniformly or in accordance with a desired pattern an electrically insulating polymerized synthetic resin substrate which is self-supporting or is secured to a support, substantially as herein described with reference to any of Examples 1 to 4.

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4. A metallized electrically insulating polymerized synthetic resin substrate, metallized by a method as claimed in any preceding Claim.

C. A. CLARK,
Chartered Patent Agent,
Century House,
Shaftesbury Avenue,
London, W.C.2.
Agent for the Applicants.

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