(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
18 October 2007 (18.10.2007)

PCT

(10) International Publication Number
WO 2007/116057 A2

(51) International Patent Classification:
D21H 19/02 (2006.01) *C23C 18/16* (2006.01)
D21H 19/08 (2006.01) *H05K 3/38* (2006.01)
C23C 26/00 (2006.01)

(21) International Application Number:
PCT/EP2007/053463

(22) International Filing Date: 10 April 2007 (10.04.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

0600805-6	10 April 2006 (10.04.2006)	SE
60/791,148	10 April 2006 (10.04.2006)	US
60/854,922	27 October 2006 (27.10.2006)	US

(71) Applicant *(for all designated States except US)*: **LINEA TERGI LTD.** [CY/CY]; P.O. Box 58341, 3733 Limassol (CY).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **HULT, Anders** [SE/SE]; Almvägen 54, S-187 34 Täby (SE). **LARSSON, Karl-Gunnar** [SE/SE]; Gammelgaarden 86, S-952 92 Kalix (SE).

(74) Agent: **BERGENSTRÅHLE & LINDVALL AB**; P.O. Box 17704, S-118 93 Stockholm (SE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) **Title:** METHOD FOR APPLYING A METAL ON A SUBSTRATE

(57) **Abstract:** There is disclosed a method for applying a first metal on a substrate, which method comprises the steps a) producing polymers on the surface of said substrate, said polymers comprising carboxylic groups and adsorbed ions of at least one second metal, said ions being adsorbed at a pH above 7, b) reducing said ions to the second metal and c) depositing said first metal on the reduced ions of said second metal. The invention further comprises objects manufactured according to the method. Advantages of the present invention include improved adhesion of the metal coating, possibility to coat many difficult materials. The process is suitable for large-scale and continuous production and it will reduce the waste of metal. Circuits manufactured according to the invention display improved signal integrity. Also there is the possibility to manufacture circuits which are built up sequentially with several layers of conductors in distinct patterns. It is also possible to manufacture of circuits with a very small line width.

WO 2007/116057 A2

Method for applying a metal on a substrate

Technical field

The present invention relates to a method for producing a metal coating on a substrate. The present invention further relates to a method of applying a distinct pattern of metal on a substrate. The present invention further relates to objects manufactured by such methods.

Background

The application of metal coatings on surfaces serves many purposes. Traditionally a coating of a noble metal was applied to an object in order to improve its appearance or to stabilise the surface. By applying metal to polymeric materials lightweight parts having an attractive appearance may be manufactured i.e. for the automobile industry.

In the case of electronic compounds and printed wire boards, a number of factors need to be considered. In addition to the adherence also the uniformity, the thickness and the resolution needs to be considered.

The application of metal coatings on surfaces serves many purposes. In electronics metal conductors are arranged on various substrates, in order to create, circuits, printed wire boards (PWB) and electronic components.

US 6,303,278 relates to a method of applying metal layers in distinct patterns. It discloses a method where the substrate surface is modified and brought into contact with monomers. The monomers will build up a polymer and conducting material is provided to the polymers and in a further step additional conducting material is added. The

step where a conducting material is added to the polymers is carried out at low pH in HCl as mentioned in the production example 1 of US 6,303,278. Several different types of monomers may be used, for instance acrylic acid. It is described as important that the substrate surface comprises secondary and/or tertiary hydrocarbon compounds. When printed wire boards are manufactured, metal is etched away from a substrate coated with a conductor. This leaves a desired pattern of conductors.

In the art several approaches have been used to improve the adhesion of metal to a substrate. For instance Yang, Shen, Li and Lu in Journal of Electronic Materials, February 1997, 26(2), pp. 78-82, have studied the adhesion of copper to parylene N. Parylene N was deposited on silicon using vapour deposition polymerisation. Copper was deposited on the parylene N film using partly ionised beam deposition. During the deposition plasma may be generated at high deposition rates and high ionisation. According to the publication the generation of plasma greatly increased the adhesion strength compared to other deposition techniques for the copper.

One problem in the state of the art concerning metal-coated objects is how to improve the adhesion of the metal coating, for a process that is applicable to many different surfaces and at the same time is economical and suitable for large-scale production. Another problem in the state of the art regarding printed wire boards is to provide a process that reduces the waste of metal, which occurs when metal is etched away from the printed wire board.

Another problem in the state of the art of manufacturing printed wire boards, is problems with under etching, difficulties in obtaining the desired resolution and difficulties in obtaining a conducting layer of uniform thickness.

Summary of the present invention

It is an object of the present invention to alleviate at least at least some of the problems in the state of the art.

The present invention is a method for applying a first metal on a substrate, which method comprises the steps:

- producing polymers on the surface of said substrate, said polymers comprising carboxylic groups and adsorbed ions of at least one second metal, said ions being adsorbed at a pH above 7,
- reducing said ions to the second metal and
- depositing said first metal on the reduced ions of said second metal.

The present invention alleviates at least some of the above-mentioned problems. In particular it improves the adhesion of the metal coating. The process is at the same time applicable to many different substrates. It is possible to use the present invention in a continuous manufacturing process. Compared to the prior art it is more economical and suitable for large-scale production because commercially available equipment can be used for large-scale use of the present invention. When using the present method for the manufacture of printed wire boards, the present method will also reduce the waste of metal that is etched away, since it is possible to use a method

where a much thinner layer is etched creating a pattern. Further metal is then added to the pattern.

The process utilises less amounts of chemicals, which in some countries are subject to regulations, compared to the traditional manufacturing methods.

Other advantages of the present invention include the properties of circuits manufactured using the present invention. Conductors on a wire board which have an hour-glass shaped cross section can be avoided and circuits with a more rectangular cross section can be manufactured with the present invention. Thus it is possible to manufacture circuits with better properties for high frequencies. The signal integrity will be improved in such circuits, compared to circuits according to the state of the art.

A further advantage is that it is possible to manufacture a conductor on a substrate with virtually the same thickness also for instance where the conductor leads from one side to another on a printed wire board. This gives improved signal integrity.

Yet another advantage is that the present method allows manufacture of circuits which are built up sequentially with several layers of conductors in distinct patterns.

Yet another advantage is that the process according to the present invention allows manufacture of circuits with a very small line width.

Definitions

Before the method for producing a metal coating on a substrate is disclosed and described, it is to be understood that this invention is not limited to particular configurations, process steps and materials disclosed herein as such configurations, process steps and materials may vary somewhat. It is also to be understood that the terminology employed herein is used for the purpose of describing particular embodiments only and is not intended to be limiting since the scope of the present invention is limited only by the appended claims and equivalents thereof.

It must be noted that, as used in this specification and the appended claims, the singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise.

In describing and claiming the present invention the following terminology will be used.

The term "initiator" as used throughout the description and in the claims denotes a substance, which has the capability to start a polymerisation reaction among monomers.

The term "latent carboxylic group" as used throughout the description and in the claims denotes a chemical group, which has the capability of being transformed into a carboxylic group.

The term "monomer" as used throughout the description and in the claims denotes a substance, which is capable of forming a polymer in a polymerisation reaction.

The term "parylene" as used throughout the description and in the claims denotes a substituted or unsubstituted poly-para-xylylene. Examples of parylene include parylene N, parylene C, and parylene D. Parylene N denotes poly-para-xylylene, parylene C denotes a parylene with an additional chlorine atom in the aromatic ring. Parylene D denotes a parylene with two additional chlorine atoms in the aromatic ring.

The term "photoinitiator" as used throughout the description and in the claims denotes an initiator, which has the capability to start a polymerisation reaction when it is exposed to light and/or UV-light.

The term "polymer" as used throughout the description and in the claims denotes a compound, which is built up of repeating identical or different structural units.

The term "polymerisation" as used throughout the description and in the claims denotes a reaction where identical or different monomers build up a polymer.

The term "polyphenylene" as used throughout the description and in the claims denotes a linear or branched polymer, which backbone comprises aromatic rings with 6 carbon atoms.

Short description of the present invention

In a first aspect the present invention relates to a method for applying a first metal on a substrate, which method comprises the steps a)producing polymers on the surface of said substrate, said polymers comprising carboxylic groups and adsorbed ions of at least one second

metal, said ions being adsorbed at a pH above 7, b) reducing said ions to the second metal and c)depositing said first metal on the reduced ions of said second metal.

In one embodiment the surface is treated using plasma before said polymers are produced. Alternatively or additionally the surface is treated in an alkaline solution. Optionally the surface is cleaned in another cleaning solution.

In one embodiment at least one primer is applied to said substrate before step a), said primer is selected from the group consisting of a polyphenylene, a cycloaliphatic polyolefin and poly(4-methyl-1-pentene).

In one embodiment the primer is parylen. In another embodiment the primer is parylen N.

In one embodiment the polymers are produced on said surface by contacting said surface with a)at least one type of monomer, of which at least one comprises a carboxylic group, b)ions of at least one second metal selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum and copper, and c)at least one initiator, and wherein the pH is above 7. The sequence in which the above mentioned ingredients are mixed is not critical.

In an alternative embodiment the polymers are produced on said surface by contacting said surface with a)at least one type of monomer, of which at least one comprises a carboxylic group, and b)at least one initiator, and thereafter contacting said surface with a solution comprising ions of at least one second metal selected from

the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum and copper, said solution having a pH above 7.

The at least one type of monomer mentioned above is in one embodiment selected from the group consisting of acrylic acid and methacrylic acid.

In another embodiment the polymers are produced on said surface by contacting said surface with a)at least one type of monomer, of which at least one comprises a latent carboxylic group, and b)at least one initiator, and thereafter subjecting said surface to conditions suitable for transforming the latent carboxylic groups into carboxylic groups, and thereafter contacting said surface with a solution comprising ions of at least one second metal selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum and copper, said solution having a pH above 7.

In one embodiment the monomer comprising a latent carboxylic group is at least one substance selected from the group consisting of tert-butyl acrylate, maleic anhydride, methacrylic anhydride and acrylic anhydride.

The conditions suitable for transforming the latent carboxylic groups into carboxylic groups, are in one embodiment achieved by contacting the surface with a photo induced Brönsted acid.

The Brönsted acid is in one embodiment selected from the group consisting of a sulfonium salt and an iodonium salt.

The initiator used as described above is in one embodiment selected from the group consisting of thioxantone, camphorquinone, benzophenone, 4-chloro benzophenone, 4,4' dichloro benzophenone, 4-benzyl benzophenone, benzoyl naphthalene, xanthone, anthraquinone, 9-fluorenone, acetophenone, benzoyl dimethylketal, hydroxy-cyclo-hexyl-acetophenone, bi-acetyl, 3,4-hexane-di-one, 2,3-pentane-di-one, 1-phenyl-1,2-propane-di-one, benzene, benzoylformic acid, formaldehyde, acetic aldehyde, acetone, 2-pentanone, 3-pentanone, cyclohexanone, methanol sulphonate esters of benzophenone and mixtures thereof.

In one embodiment the ions of the at least one second metal are palladium ions and the method further comprises ammonium ions. The ammonium ions are in this particular embodiment in the same solution as the palladium ions.

In one embodiment the ions are adsorbed at a pH above 10.

In one embodiment the first metal is selected from the group consisting of copper, silver, gold, nickel, titanium, and chromium.

In a particular embodiment the surface is further subjected to the steps of d) selectively depositing a third metal to said surface in a distinct pattern, and e) removing said first and second metal from said surface on the parts which are not covered by said third metal.

In one particular embodiment the third metal is copper.

In an alternative embodiment the metal is applied in a distinct pattern on said substrate. This is achieved by

performing any one or several of the steps outlined in claim 1 in the desired distinct pattern on said substrate.

In yet another alternative embodiment the metal is applied on the entire substrate. In this embodiment the metal is preferably but not necessarily applied in a uniform layer.

In a second aspect the present invention encompasses an object manufactured according to the method described herein.

In one embodiment the object has a thickness of the layer of the first metal from about 2µm to about 5µm.

In one embodiment the object comprises electrical circuits. In one embodiment the object is a printed wire board.

In one embodiment the object comprises more than one layer of conductors electrically insulated from each other. This is an SBU process.

The present invention relates to a new method of applying a first metal on a substrate, which is made of any material. The object to be coated can, as far as the inventors presently are aware of, be made of any material. Preferably the material to be coated is halogen free. Examples of materials which have been tested and found to give good adhesion of applied metal include Teflon® (Polytetrafluoroethylene), ceramic materials, glass, epoxy resins, paper coated with PET and metal. Other examples of suitable materials for substrates according to the present invention include various polymers comprising carbon and hydrogen atoms. Other examples of objects suitable to be

coated are glass fibre reinforced disks in an epoxy resin or in another suitable polymeric material. Substrates from different manufacturers have successfully been coated according to the present invention. Those manufacturers include Isola, Matsushita, Arlon, Rogers and Polyclad.

Detailed description of the present invention

These steps according to the method of the present invention will now be explained in greater detail.

The object to be coated is preferably clean, when the process is started.

The object to be coated is in one embodiment first treated with plasma. The treatment makes it possible to wet objects which otherwise are difficult adhere to. The plasma treatment also has a cleaning effect. The plasma treatment may be conducted in any gas that gives a polar surface and at any suitable pressure. In one embodiment of the present invention the plasma treatment is carried out at ambient pressure in air. The present inventors have found that treatment with plasma in combination with the rest of the method as described herein gives excellent results. Although an initial plasma treatment is preferred, it should be noted that for some objects a plasma treatment is not mandatory. As an alternative to plasma a cleaning in an alkaline solution is sufficient for some substrates.

After the plasma treatment a primer is optionally applied to at least a part of the surface of the object. Non-limiting examples of a primer are a polyphenylene, and a cycloaliphatic polyolefin. Examples of cycloaliphatic polyolefins include copolymers made from ethylene and

norbornene. Further more specific examples of a primer include poly(4-methyl-1-pentene), parylene N, parylene C, parylene D, parylene F, parylene A, parylene AM, and parylene HT. Parylene is preferably applied from the gas phase. Application devices for parylene are commercially available and a person skilled in the art can apply a layer of a parylene. The thickness of the primer layer can vary within wide boundaries. In one embodiment the layer is thinner than 100 µm, and in another embodiment the layer is from about 2 to about 20 µm.

After the application of a primer, a metal is applied on the primer. There are several approaches for applying a metal on the polyphenylene. In one embodiment the application of a metal comprises the application of a polymer on the surface. The inventors have discovered that the method with application of a polymer on the surface gives excellent results together with a primer selected from the group consisting of a polyphenylene, a cycloaliphatic polyolefin and poly(4-methyl-1-pentene). In one embodiment of the present invention a polymer is grafted on a polyphenylene.

The polymer on the surface comprises carboxylic groups. There are several approaches for achieving carboxylic groups on the polymers. Examples of such approaches are described more in detail below.

In one embodiment of the present invention monomers comprising carboxylic groups are used to build up the polymer with the aid of an initiator for the polymerisation reaction. It is also possible to use a mixture of different monomers, i.e. a mixture comprising

monomers containing carboxylic groups and monomers that do not contain carboxylic groups.

In another embodiment of the present invention monomers with latent carboxylic groups are incorporated when building up the polymer on the object. The polymer can be entirely built up of monomers comprising latent carboxylic groups. Alternatively the polymer can be built up of both monomers comprising latent carboxylic groups and monomers without latent carboxylic groups. The polymer on the object is then subjected to conditions such that the latent carboxylic groups in the polymers are transformed into carboxylic groups.

One non limiting example of a latent carboxylic group is maleic anhydride. If maleic anhydride is used as a monomer it is incorporated in the polymer during the polymerisation and is then subjected to conditions such that it is transformed into carboxylic groups. In another embodiment of the present invention a latent carboxylic acid such as tert-butyl acrylate is used to build up a polymer, where after it is transformed into a carboxylic group using suitable conditions. Another example of a latent carboxyl group is a protected carboxy group.

A non limiting example of a suitable condition for transformation of latent carboxylic groups into carboxylic groups is treatment with a Brönsted acid. In one embodiment of the present invention the Brönsted acid is produced in a photoreaction, i.e. a photo induced Brönsted acid. Non-limiting examples of Brönsted acids are sulfonium salts and iodonium salts. A person skilled in the art realises that there are several ways of transforming a latent carboxylic group into a carboxylic

group. Maleic anhydride can for instance be transformed into maleic acid by heat treatment.

In all of the above-described different approaches to produce polymers comprising carboxylic groups, at least one initiator is used to initiate the polymerisation reaction. The initiator can either be a photoinitiator or another initiator. When a photoinitiator is used it is understood that the method also encompasses irradiation with light of a suitable wavelength. Examples of suitable photoinitiators are compounds comprising carbonyl groups, such as aromatic ones. Aromatic ketones and aromatic aliphatic ketones absorb electromagnetic waves, especially in the interval of about 200 to about 500 nm, making these compounds useful as initiators according to the invention. In one embodiment of the present invention the initiator according to the present invention is chosen from the group consisting of said initiator is selected from the group consisting of thioxantone, camphorquinone, benzophenone, 4-chloro benzophenone, 4,4' dichloro benzophenone, 4-benzyl benzophenone, benzoyl naphthalene, xanthone, anthraquinone, 9-fluorenone, acetophenone, benzoyl dimethylketal, hydroxy-cyclo-hexyl-acetophenone, bi-acetyl, 3,4-hexane-di-one, 2,3-pentane-di-one, 1-phenyl-1,2-propane-di-one, benzene, benzoylformic acid, formaldehyde, acetic aldehyde, acetone, 2-pentanone, 3-pentanone, cyclohexanone, methanol sulphonate esters of benzophenone and mixtures thereof.

The carboxylic groups of the polymers have adsorbed metal ions. The metal ions are always adsorbed at a pH above 7. Below there are provided alternative approaches for adsorbing the ions onto the polymers:

In a first approach the ions of said second metal are mixed together with the monomers before the polymerisation takes place. In a second approach the ions are added in a subsequent step when the polymers already are produced on the surface. The first approach when the ions of the second metal are added to the monomer solution has one step less.

In the first approach the solution of monomers comprises ions of at least one second metal selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum and copper. The amount of ions of the second metal may vary within a broad interval. A non-limiting example of a suitable amount of ions is approximately one metal ion with the charge +2 per two monomer molecules with the charge -1.

In the second approach the surface of the object is contacted with a solution comprising ions of a second metal. The second metal is at least one metal selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum and copper. For the second approach with a separate adsorption step for ions of the second metal, the present inventors have found that in contrast to the state of the art described in US 6,303,278, the solution should have a pH value above 7. The higher pH value as compared to the known prior art leads to a better adhesion of the metal layer. In one embodiment of the present invention the pH value is about 11. In another embodiment of the present invention the pH value is about 11.5. In another embodiment of the present invention the pH value is above 10. In another embodiment of the present invention the pH value is above 9. In

another embodiment of the present invention the pH value is above 8.

In another embodiment of the present invention, the solution comprising ions of a second metal further comprises ammonium ions. In another embodiment of the present invention the solution comprising ions of a second metal comprises palladium ions and ammonium ions. A person skilled in the art realises that counter-ions have to be present.

Ions of the second metal, which are bound to the polymer, are reduced to said second metal. This reduction is carried out irrespectively of which approach has been used to apply the metal ions to the polymers. In one embodiment of the present invention the reduction is achieved with a chemical reaction using a reducing solution for instance sodium borohydride. In one embodiment of the present invention the reduction comprises a photochemical reaction. In another embodiment of the present invention the reduction involves a thermal treatment. A person skilled in the art can in the light of this description realise several ways to reduce metal ions to metal. Thus also other ways of reducing the metal ions can be used within the scope of the present invention.

When the ions of the second metal have been reduced to metallic form and after an optional second plasma treatment the first metal is deposited on the surface by contacting it with a solution comprising ions of the first metal. In one embodiment of the present invention the solution comprises ions of the first metal, a complexing agent and a reduction agent. In one embodiment of the present invention the solution for depositing the first

metal is a standard solution that is commercially available. In one embodiment of the present invention the thickness of the layer of the first metal is below 100µm. In another embodiment of the present invention the thickness is in the range 0.25-40µm, in another embodiment of the present invention the thickness is in the range 0.5-20µm, in another embodiment of the present invention the thickness is in the range 1-10µm and in another embodiment of the present invention the thickness is in the range 2-5µm.

In one embodiment the substrate is heated after the application of the metal in order to evaporate undesired substances and gases formed during the process. If the substrate is temperature sensitive it should not be heated too much. In one embodiment the maximum temperature is below the glass transition temperature or melting temperature of the substrate. In one embodiment the maximum temperature is below 130°C, in another embodiment the maximum temperature is below 100°C. The duration of the heat treatment is not critical. Examples of duration times range from a few seconds to several hours. Typically the duration of the heat treatment is within the interval from a few minutes to about 30 minutes.

The objects coated with metal according to the present invention may be used in many contexts. One application according to the present invention of a substrate coated with metal is described below. Usually printed wire boards are manufactured from boards coated with a layer of a metal, which metal then selectively is removed leaving a desired pattern of conducting metal. This is a well-known and widely used technology

In one embodiment of the present invention a board coated with a metal layer without any pattern according to the present invention is used for the manufacture of a printed wire board. The metal layer is thinner compared to the metal-coated substrates that conventionally are used for manufacturing printed wire boards. Further metal is deposited with electroplating to the surface in a desired pattern. In one embodiment the surface is covered with a mask and further metal is deposited in a distinct pattern determined by the mask. The mask is then removed. This creates a board with a thin coating of a metal and a distinct pattern thereon consisting of a thicker metal coating. The board is then subjected to etching for a time that is sufficiently long to etch away the thin coating but sufficiently short to leave the pattern consisting of the thick coating. A person skilled in the art can in the light of this description and the claims determine a suitable etching time. This gives a printed wire board with a desired distinct pattern of metal on the substrate.

The process according to the present invention has many advantages. One advantage is improved adhesion and the possibility to apply metal on many different types of substrates. Another advantage is that less metal is needed to produce the metallized substrates for the printed wire board industry. As a consequence less metal needs to be removed by etching in the first step of manufacturing. Further the problems of “hour-glass” shaped conductors and “under-etching”, due to the etching liquid acting not only on the surface but also on the sides of the conductors, are eliminated. This makes it possible to produce narrower conductors and thus produce more compact printed wire boards. It is also possible to use existing technology and existing production lines with only minor modifications to

manufacture these printed wire boards because the conventional metal-coated substrates are replaced by improved metal-coated substrates according to the present invention.

With the new method of manufacturing substrates with a thin metal coating according to the present invention it is now possible to utilize the above-described method of manufacturing printed wire boards. This has not been possible before because the adhesion of metal has not been sufficient and the method has not been suitable for large-scale production.

An alternative use of substrates according to the present invention for the manufacture of circuits is to apply the metal in a distinct pattern on a substrate. This is in one embodiment achieved by applying the reagents in the desired pattern. In an alternative embodiment this is achieved by irradiation in the desired pattern. In a specific form of this embodiment this is achieved by creating a photo induced Brönsted acid in a distinct pattern on the substrate.

In one embodiment of the present invention a SBU procedure is used. The present invention encompasses use of a sequential build-up (SBU). In this embodiment a desired pattern of conductors is applied on a substrate, where after an insulating layer is applied. On the insulating layer another desired pattern of conductors are applied. This process is repeated until the desired number of layers with conductors are achieved. Contact between the conductors in the different layers is achieved by methods known to a person skilled in the art of printed wire boards.

Other features of the invention and their associated advantages will be evident to a person skilled in the art upon reading the description and the examples.

It is to be understood that this invention is not limited to the particular embodiments shown here. The following examples are provided for illustrative purposes and are not intended to limit the scope of the invention since the scope of the present invention is limited only by the appended claims and equivalents thereof.

Examples

Example 1

A substrate of halogen free epoxy resin was subjected to plasma treatment in a plasma reactor in air at ambient pressure for 1 minute. After the plasma treatment the substrate was coated with a 3µm thick layer of parylene N (poly-para-xylylene). The raw material for the parylene coating was heated to the gas phase at about 150°C. During a pyrolysis step at about 650°C the gas becomes a reactive monomer gas. The poly-para-xylylene forms on the substrate at about room temperature in vacuum. This parylene coating method is well known. After the coating with parylene N polymers were grafted onto the parylene using the following steps. The substrate was contacted with a solution prepared according to the following. $PdCl_2$ was dissolved in acrylic acid in an amount corresponding to one Pd^{2+}-ion per two molecules of acrylic acid. The solution was diluted 20 times with methanol and thioxantone was added to a final concentration of 0.01wt%. The solution was mixed thoroughly before it was contacted with the substrate. After contacting the substrate with

the solution the substrate was dried to evaporate the methanol. Thereafter it was irradiated with UV-light for 10 seconds and the polymerisation reaction was allowed to proceed for 4 minutes. The substrate was rinsed in running water for 30 seconds. Then the palladium ions, which were adsorbed to the polymers, were reduced by contacting the substrate with a freshly made aqueous solution of 1wt% $NaBH_4$. Thereafter the substrate was rinsed in running water for 30 seconds. After this step the substrate was contacted with an autocatalytic bath for deposition of copper. The bath was an aqueous standard bath for the deposition of copper comprising $CuSO_4$, EDTA (ethylenediaminetetra-acetic acid), HCHO, and NaOH. The pH value was 11.7 and the temperature was 35°C. After the copper deposition the substrate was rinsed in running water for 30 seconds and dried. This yielded an epoxy resin with a 2 µm thick coating of copper. Adhesion was tested by applying a piece of adhesive tape to the surface and then quickly tearing it away. No copper was removed and thus the adhesion was deemed to be excellent.

Example 2

A substrate of halogen free epoxy resin was subjected to plasma treatment in a plasma reactor in air at ambient pressure for 1 minute. After the plasma treatment the substrate was coated with parylene N using the method according to example 1. After the parylene coating the substrate was contacted with a solution comprising 1 wt% acrylic acid and 0.01wt% thioxantone. The substrate was irradiated with UV-light for 10 seconds and the polymerisation reaction was allowed to proceed for 4 minutes. The substrate was rinsed in running water for 30 seconds. The polymerisation reaction yielded a polymer with covalent bonds to the surface, i.e. grafted to the

surface. The substrate was then contacted for 30 seconds with an aqueous solution of 0.48wt% of $PdCl_2$ and 5.2wt% of a concentrated aqueous NH_3-solution. Thus the solution comprised ammonium ions (NH_4^+). The pH of the solution was adjusted with an aqueous NH_3-solution to 11.5. The substrate was then rinsed in running water for 30 seconds. Then the palladium ions, which were adsorbed to the polymers, were reduced by contacting the substrate with a freshly made aqueous solution of 1wt% $NaBH_4$. Thereafter the substrate was rinsed in running water for 30 seconds. After this step the substrate was contacted with an autocatalytic bath for deposition of copper. The bath was an aqueous standard bath for the deposition of copper comprising $CuSO_4$, EDTA (ethylenediaminetetra-acetic acid), HCHO, and NaOH. The pH value was 11.7 and the temperature was 35°C. After the copper deposition the substrate was rinsed in running water for 30 seconds and dried. The substrate was heated to about 100°C during 15 minutes in order to evaporate undesired substances from the substrate. This yielded an epoxy resin with a 2 µm thick coating of copper. Adhesion was tested by applying a piece of adhesive tape to the surface and then quickly tearing it away. No copper was removed and thus the adhesion was deemed to be excellent.

Example 3-4

The procedure of example 2 was repeated but the concentration of acrylic acid was 2wt% and 7wt% respectively. This yielded an epoxy resin with a 2 µm thick coating of copper. The adhesion was tested as in example 2. All of the copper coating remained on the object and thus the adhesion was deemed to be excellent.

Example 5

The procedure of example 2 was repeated but $PdCl_2$ was replaced by $CuCl_2$. It turned out that the subsequent deposition of metal was considerably slower than in example 2 but this nevertheless eventually yielded an epoxy resin with a 2µm thick coating of copper. The adhesion was tested as in example 2. All of the copper coating remained on the object and thus the adhesion was deemed to be excellent.

Example 6

The procedure of example 2 was repeated but the aqueous solution of $PdCl_2$ and NH_3 was diluted 10 times compared to example 2. The pH value was adjusted to 11.5 by adding a concentrated aqueous solution of NH_3. It was necessary to add more of the aqueous solution of NH_3 compared to example 2 to obtain a pH of 11.5. This still yielded an epoxy resin with a 2 µm thick coating of copper. The adhesion was tested as in example 2. All of the copper coating remained on the object and thus the adhesion was deemed to be excellent.

Example 7

The procedure of example 2 was repeated but the autocatalytic bath comprising copper was allowed to act for a shorter time, which yielded a 0.5µm thick coating of copper. The adhesion was tested as in example 2. All of the copper coating remained on the object and thus the adhesion was deemed to be excellent.

Example 8

The procedure of example 2 was repeated but the temperature of the autocatalytic bath comprising copper was lowered to 30°C and the bath was allowed to act for 12

hours, which yielded a 15µm thick coating of copper. The adhesion was tested as in example 2. All of the copper coating remained on the object and thus the adhesion was deemed to be excellent.

Example 9-10

The procedure of example 2 was repeated but the pH of the aqueous solution comprising palladium ions and ammonium ions was adjusted to 10.5, 11.0 and 12.0 respectively. This yielded an epoxy resin with a 2 µm thick coating of copper. The adhesion was tested as in example 2. All of the copper coating remained on the object and thus the adhesion was deemed to be excellent.

Example 12

A substrate of halogen free epoxy resin coated with copper according to example 2 was covered with a mask determining a desired conductor pattern. Copper was deposited to the parts of the board, which were not covered by the mask using standard electroplating to a thickness of 20-25µm. After the addition of copper the mask was removed and the board was rinsed in running water for 30 seconds. After this step the board had a distinct pattern consisting of approximately 20-25µm thick copper and the space between the parts with 20-25µm thick copper had a 2µm thick coating of copper. Then the entire board was subjected to an etching bath. Copper was etched away from the entire surface. The 2µm thick copper was quickly etched away and thereafter the etching was interrupted, leaving the distinct pattern of copper. The waste of copper was reduced compared to a traditional method.

Example 13

Example 2 was repeated but the substrate consisted of Teflon (polytetrafluoroethylene). The adhesion of the copper was tested as in example 2 and deemed to be excellent.

Example 14

Example 2 was repeated but the substrate consisted of glass. The adhesion of the copper was tested as in example 2 and deemed to be excellent.

Example 15

Example 2 was repeated but the substrate consisted of a ceramic material (?). The adhesion of the copper was tested as in example 2 and deemed to be excellent.

Example 16

Example 2 was repeated but the substrate consisted of paper coated with PET (Polyethyleneterephtalate). The adhesion of the copper was tested as in example 2 and deemed to be excellent.

Example 17

Example 2 was repeated but the thickness of parylene N was 20µm. The adhesion of the copper was tested as in example 2 and deemed to be excellent.

Example 18

Example 2 was repeated but the thickness of parylene N was 2µm. The adhesion of the copper was tested as in example 2 and deemed to be excellent.

Example 19

A substrate of halogen free epoxy resin was thoroughly rinsed in an alkali solution and then rinsed in water and dried. The substrate was contacted with a solution comprising 1 wt% acrylic acid and 0.01wt% thioxantone. The substrate was irradiated with UV-light for 10 seconds and the polymerisation reaction was allowed to proceed for 4 minutes. The substrate was rinsed in running water for 30 seconds. The polymerisation reaction yielded a polymer with covalent bonds to the surface, i.e. grafted to the surface. The substrate was then contacted for 30 seconds with an aqueous solution of 0.48wt% of $PdCl_2$ and 5.2wt% of a concentrated aqueous NH_3-solution. Thus the solution comprised ammonium ions (NH_4^+). The pH of the solution was 11.5. The substrate was then rinsed in running water for 30 seconds. Then the palladium ions, which were adsorbed to the polymers, were reduced by contacting the substrate with a freshly made aqueous solution of 1wt% $NaBH_4$. Thereafter the substrate was rinsed in water for 30 seconds. After this step the substrate was contacted with an autocatalytic bath for deposition of copper. The bath was an aqueous standard bath for the deposition of copper comprising $CuSO_4$, EDTA (ethylenediaminetetra-acetic acid), HCHO, and NaOH. The pH value was 11.7 and the temperature was 35°C. After the copper deposition the substrate was rinsed in running water for 30 seconds and dried. The substrate was dried. This yielded an epoxy resin with a 2 µm thick coating of copper.

Five different samples were manufactured using the method above and the same type of substrate. The adhesion was tested with a 90° peel tester and the following results were obtained.

Peel strength (N/cm)
11.7
13.2
12.4
10.9
10.4

Claims

1. A method for applying a first metal on a substrate, which method comprises the steps
   a. producing polymers on the surface of said substrate, said polymers comprising carboxylic groups and adsorbed ions of at least one second metal, said ions being adsorbed at a pH above 7,
   b. reducing said ions to the second metal and
   c. depositing said first metal on the reduced ions of said second metal.

2. The method according to claim 1, wherein said surface is treated using plasma before said polymers are produced.

3. The method according to any one of claims 1-2, wherein at least one primer is applied to said substrate before step a), said primer is selected from the group consisting of a polyphenylene, a cycloaliphatic polyolefin and poly(4-methyl-1-pentene).

4. The method according to claim 3, wherein said primer is parylen.

5. The method according to claim 3, wherein said primer is parylen N.

6. The method according to any one of claims 1 to 5, wherein said polymers are produced on said surface by contacting said surface with
   - at least one type of monomer, of which at least one comprises a carboxylic group,
   - ions of at least one second metal selected from the group consisting of ruthenium, rhodium,

palladium, osmium, iridium, platinum and copper, and

- at least one initiator,

and wherein the pH is above 7.

7. The method according to any one of claims 1 to 5, wherein said polymers are produced on said surface by contacting said surface with

- at least one type of monomer, of which at least one comprises a carboxylic group, and
- at least one initiator,

and thereafter contacting said surface with a solution comprising ions of at least one second metal selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum and copper, said solution having a pH above 7.

8. The method according to any one of claim 6 or 7, wherein said at least one type of monomer is selected from the group consisting of acrylic acid and methacrylic acid.

9. The method according to any one of claims 1 to 5, wherein said polymers are produced on said surface by contacting said surface with

- at least one type of monomer, of which at least one comprises a latent carboxylic group, and
- at least one initiator,

and thereafter subjecting said surface to conditions suitable for transforming the latent carboxylic groups into carboxylic groups,
and thereafter contacting said surface with a solution comprising ions of at least one second metal selected from the group consisting of ruthenium, rhodium,

palladium, osmium, iridium, platinum and copper, said solution having a pH above 7.

10. The method according to claim 9, wherein said monomer comprising a latent carboxylic group is at least one substance selected from the group consisting of tert-butyl acrylate, maleic anhydride, methacrylic anhydride and acrylic anhydride.

11. The method according to claim 9 or 10 wherein said conditions suitable for transforming the latent carboxylic groups into carboxylic groups, are achieved by contacting the surface with a photo induced Brönsted acid.

12. The method according to claim 11 where in said Brönsted acid is selected from the group consisting of a sulfonium salt and an iodonium salt.

13. The method according to any one of claims 6 to 12, wherein said initiator is selected from the group consisting of thioxantone, camphorquinone, benzophenone, 4-chloro benzophenone, 4,4' dichloro benzophenone, 4-benzyl benzophenone, benzoyl naphthalene, xanthone, anthraquinone, 9-fluorenone, acetophenone, benzoyl dimethylketal, hydroxy-cyclo-hexyl-acetophenone, bi-acetyl, 3,4-hexane-di-one, 2,3-pentane-di-one, 1-phenyl-1,2-propane-di-one, benzene, benzoylformic acid, formaldehyde, acetic aldehyde, acetone, 2-pentanone, 3-pentanone, cyclohexanone, methanol sulphonate esters of benzophenone and mixtures thereof.

14. The method according to any one of claims 1-13, wherein said ions of at least one second metal are

palladium ions and said method further comprises ammonium ions.

15. The method according to any one of claims 1-14, wherein said ions being adsorbed at a pH above 10.

16. The method according to any one of claims 1 to 15, wherein said first metal is selected from the group consisting of copper, silver, gold, nickel, titanium, and chromium.

17. The method according to any one of claims 1 to 16, wherein said surface is further subjected to the steps of

d. selectively depositing a third metal to said surface in a distinct pattern, and

e. removing said first and second metal from said surface on the parts which are not covered by said third metal.

18. The method according to any one of claims 1 to 16, wherein said metal is applied in a distinct pattern on said substrate.

19. The method according to any one of claims 1 to 16, wherein said metal is applied on the entire substrate.

20. The method according to claim 17, wherein the third metal is copper.

21. An object comprising a substrate manufactured according to any one of claims 1 to 20.

22. The object according to claim 21, wherein the thickness of the layer of said first metal is from about 2µm to about 5µm.

23. The object according to any one of claims 21 to 22, wherein said object comprises a circuit.

24. The object according to any one of claims 21 to 23, wherein said object is a printed wire board.

25. The object according to any one of claims 21 to 24, comprising more than one layer of conductors electrically insulated from each other.