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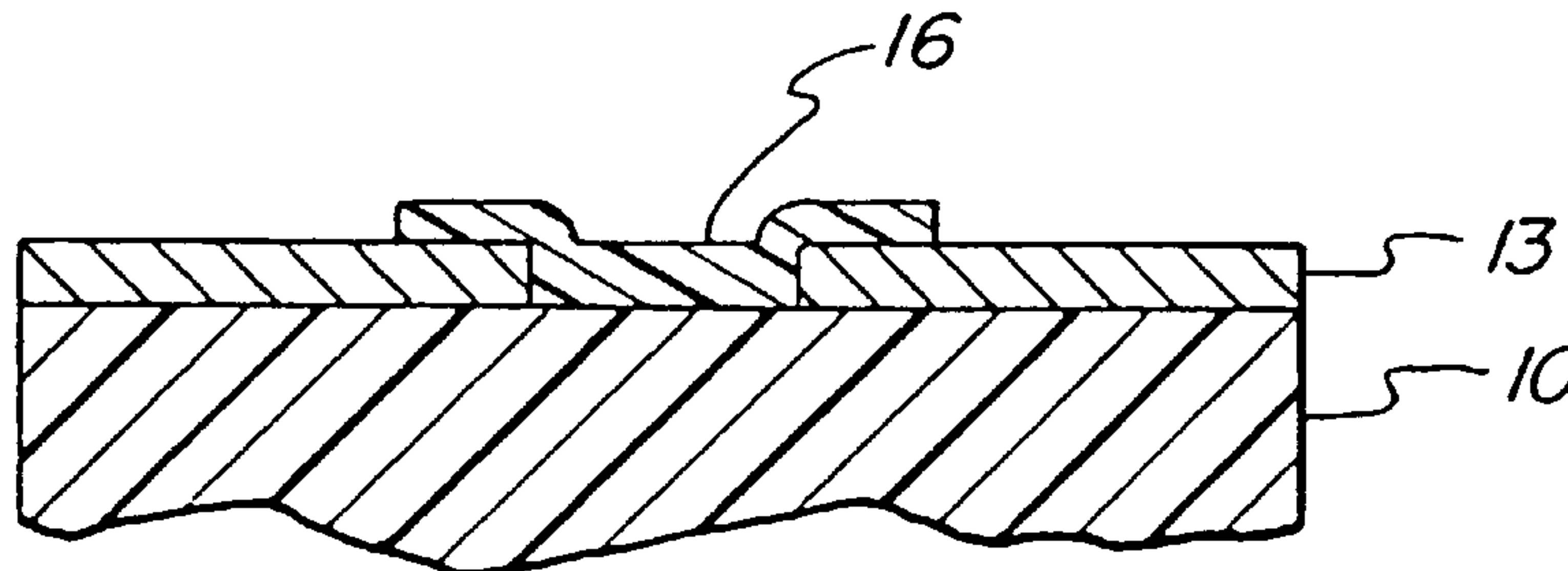
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A process and product manufactured by the process is revealed whereby resistors (16) can be manufactured integral a printed circuit board (10, 13) by plating the resistors onto an insulative substrate (10). Uniformization of the insulative substrate by etching and oxidation of the plated resistor are revealed as techniques for improving the uniformity and consistency of the plated resistors.



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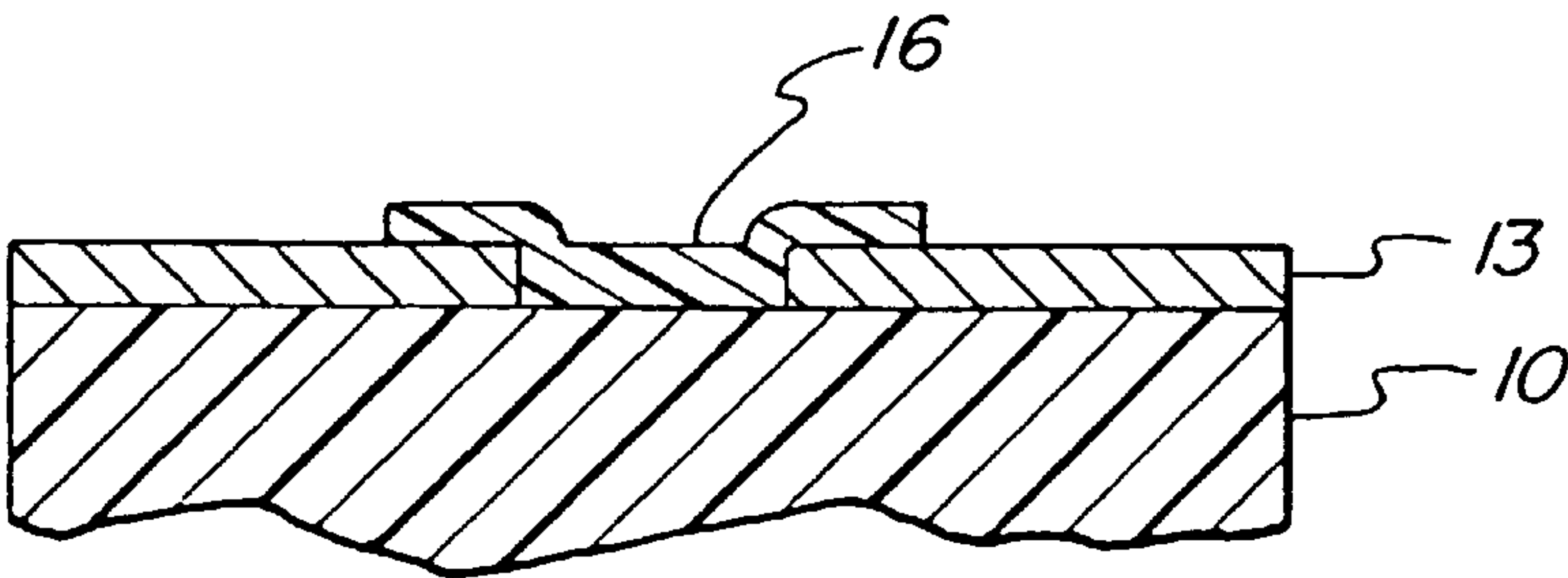
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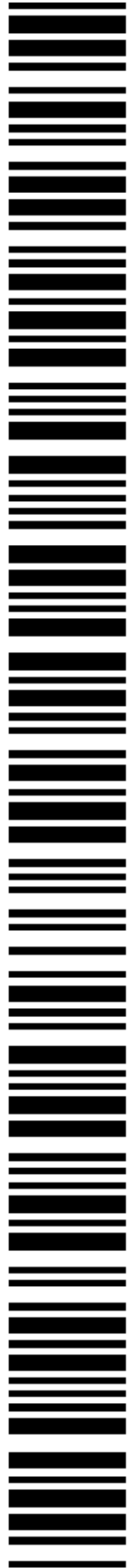
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(54) Title: PROCESS FOR THE MANUFACTURE OF PRINTED CIRCUIT BOARDS WITH PLATED RESISTORS



(57) Abstract: A process and product manufactured by the process is revealed whereby resistors (16) can be manufactured integral a printed circuit board (10, 13) by plating the resistors onto an insulative substrate (10). Uniformization of the insulative substrate by etching and oxidation of the plated resistor are revealed as techniques for improving the uniformity and consistency of the plated resistors.



WO 02/01636 A1

**Process for the Manufacture of Printed Circuit Boards
with Plated Resistors**

5 This application is a continuation – in – part of U. S. Patent Application No. 08/732,649 filed on October 16, 1996 and which is currently pending.

Field of Invention

10 The present invention relates to a process for the manufacture of double-sided or multilayer printed circuit boards with printed plated resistors. The method proposed produces printed circuits with integral resistors which are printed and plated in place on the surfaces of the printed circuit board. The process produces printed circuit boards with resistors in a manner that is more efficient and economical than previously possible.

15

Background of the Invention

20 In the manufacture of printed circuits, it is now commonplace to provide planar boards having circuitry on each side thereof (e.g. double-sided circuit boards). It is also commonplace to produce boards comprised of integral planar laminates of insulating substrate and conductive metal, wherein one or more parallel innerlayers or planes of the conductive metal, separated by insulating substrate, are present within the structure with the exposed outer surfaces, along with the inner planes, of the laminate containing printed circuit patterns (e.g. 25 multilayer circuit boards).

30 In double sided and multilayer circuit boards, it is necessary to provide interconnection between or among the various layers and/or sides of the board containing the conductive circuitry. This is achieved by providing metalized, conductive thru-holes in the board communicating with the sides and layers requiring electrical interconnection. The predominantly employed method for providing conductive thru-holes is by electroless deposition of metal on the non-conductive surfaces of the thru-holes which have been drilled or punched through the board. Typically the electroless deposition is followed by electrolytic

deposition of metal in the holes to build conductive metal to the required thickness. Recently some processes have allowed for direct electroplating in the thru-holes without need for prior electroless deposition.

5 The typical manufacturing sequence for producing printed circuit boards begins with a copper-clad laminate. The copper clad laminate comprises a glass reinforced epoxy insulating substrate with copper foil adhered to both planar surfaces of said substrate, although other types of insulating substrates such as paper phenolic and polyimide, have been used. First the thru-holes are drilled or
10 punched in the copper clad laminate thereby exposing the hole surfaces of insulating substrate material. The holes are then subjected to a chemical plating process which deposits conductive metal in the holes as well as on the copper surfaces. A plating mask is provided on the outer surfaces in the negative image of the circuitry desired. Subsequently copper is electroplated on all surfaces, not
15 covered by the plating mask, to a predetermined thickness, followed by a thin deposition of tin to act as an etch resist. The plating resist is then stripped and the exposed copper surfaces (i.e., those not plated with the etch resist) are etched away. Finally the etch resist is removed and printed circuit board is finished with one of a number of known finishing methods such as solder mask, followed by hot air
20 solder leveling. The foregoing process is typically called the pattern plate process and is suitable for producing double-sided printed circuit boards or multilayer boards. However in the case of multilayer boards, the starting material is a copper clad laminate which comprises inner planes of circuitry called innerlayers.

25 Simple printed circuit boards and the innerlayers of a multilayer circuit board are produced through a technique called print and etch. In this manner a photopolymer is laminated or dried on the copper surfaces of a copper clad laminate. The photopolymer is then selectively imaged using a negative and developed to produce a positive image of the desired circuit pattern on the surfaces
30 of the copper clad laminate. The exposed copper is then etched away and the photopolymer stripped, revealing the desired circuit pattern.

The semi-additive process may be used in conjunction with the print and etch process to produce double sided or multilayer print and etch boards with plated thru-holes. In this process a copper clad laminate or a multilayer package with copper foil on the exterior surfaces is processed through the print and etch process as given above. Holes are then drilled in the board in a desired array. A plating resist is then applied to cover substantially the entire outer surfaces of the board except for the holes and the circuits. The exposed areas are then plated electrolessly.

10 In addition to the foregoing, many other processes have been utilized to produce printed circuit boards. Some of these processes are detailed in U.S. Patent Nos. 3,982,045, 4,847,114 and 5,246,817, the teachings each of which are incorporated herein by reference in their entirety. However, in the prior art processes, the circuits are made such that resistors, if required, need to be provided
15 externally from the circuit board itself. (e.g. mounted on the surface of the circuit board as an appendage).

The inventors herein have discovered a process whereby resistors can be printed and plated as an integral part of the circuitry of the printed circuit board.
20 This provides for an efficient and economical way of providing the necessary resistors. In addition the process provides for further miniaturization of the printed circuit boards produced in comparison to those produced by prior art methods. Typical prior art in this regard are U.S. Patent Nos. 3,808,576 and 2,662,957, the teachings both of which are incorporated by reference herein in their entirety.

25

In its preferred embodiment, the invention produces printed circuits with integral resistors, which resistors have a particularly constant resistance as is required by the most demanding applications.

30

Brief Description of the Figures

Collectively the figures visually show the steps of the basic process of this invention.

5 Figure 1A represents one side of the copper clad laminate (although both sides would most likely be processed in the same way) with insulating dielectric substrate, 10, and the attached copper foil, 11.

 Figure 1B indicates the presence of an imaged resist, 12, on the copper foil, 11. The resist, 12, has already been imaged and developed and therefore covers only the desired portions of the copper foil, 11.

 Figure 1C indicates that the exposed copper has now been etched away leaving unconnected resist covered copper traces, 13 and 14 on the substrate, 10.

15

 Figure 1D indicates that the resist has now been completely stripped away leaving only the desired copper traces, 13 and 14 on the substrate, 10.

 Figure 1E shows the application of a plating resist, 15, which covers the entire area of the board except the portions where the resistor will be plated.

20

 Figure 1F shows the plated resistor, 16, connecting the previously unconnected copper traces, 13 and 14.

25 Figure 1G shows the circuit after the plating resist has been stripped away.

Summary of the Invention

 The current invention proposes a process for printing and plating resistors as an integral part of a printed circuit board. The foregoing process is described in its basic form by the following sequence of processing steps:

30

- 5
- a). Apply an etch resist on the surface of a metal clad laminate (or multilayer package) in a desired pattern. The desired pattern should preferably define the conductive circuits desired in a positive manner and should define the areas between the circuits and locations for the resistors in a negative manner;
 - b). Etch away the exposed copper and preferably remove the etch resist;
 - c). Activate the surfaces to accept plating thereon;
 - d). Apply a plating mask which covers substantially all of the surfaces except for the areas where the resistors are to be plated;
 - 10 e). Plate the exposed areas with a resistive material; and
 - f). Strip away the plating mask.

As an equivalent to the foregoing process, foregoing steps a and b can be replaced by an additive process with the following steps:

- 15
- a.1.). Activate the surfaces of a bare dielectric substrate to accept plating thereon;
 - a.2.). Apply a plating mask to the dielectric substrate such that the desired circuits are defined in a negative manner and the areas between the circuits and the locations for the resistors
 - 20 are defined in a positive manner;
 - a.3.) Plate the desired circuitry;
 - a.4.) Strip away the plating resist; and

Subsequently follow steps (c) through (f) noted previously.

25

In a preferred embodiment the substrate is subjected to a dielectric etchant after step b but before step c in order to uniformize the dielectric surface. The inventors have found that etching at this point to uniformize the dielectric surface will provide plated resistors with more constant and predictable resistance.

30

In another preferred embodiment, the plated resist material is contacted with an oxidant between steps (e) and (f) or after step (f). The inventors have found that contacting the plated resist material with an oxidant, and thereby oxidizing the plated resist material in a controlled manner provides plated resistors
5 with more constant and predictable resistance and optionally with higher resistance if desired. Intrinsic resistance increases via controlled oxidation.

In a third preferred embodiment, the printed circuit board is subjected to a cleaning step after step (f) in order to remove any residual activator species from
10 step (c) and to otherwise improve the surface insulation resistance of the board in general. The inventors have found the inclusion of this step to produce printed circuit boards in this regard with higher reliability.

Detailed Description of the Invention

15 The processes described herein provide a method of forming a resistor between two conductive areas, which areas are upon and separated by an insulating substrate. The method described provides for plating a resistive material onto the insulating substrate, which is between the conductive areas, such that the resistive material connects the conductive areas. The processes described are particularly
20 useful in producing printed circuit boards with plated resistors which are integral with the circuits. The most basic processing sequence is described as follows:

- a). apply an etch resist onto the surfaces of a metal clad laminate such that the resist defines the desired circuitry in a positive manner and
25 the areas between the circuits including the locations for the resistors are defined in a negative manner;
- b). etch away exposed copper surfaces and strip the resist;
- c). optionally, treat the exposed dielectric surfaces with a process selected from the group consisting of chemical etching, plasma
30 etching, laser normalization, vapor blasting, sanding, shot blasting and sand blasting;

- d). activate the exposed dielectric surfaces to accept plating thereon;
- e). apply a plating mask such that the plating resist covers all or substantially all of the surfaces except for the areas where the resistors are to be plated (i.e. such that the resistor areas are defined
- 5 in a negative manner;
- f). plate the exposed areas;
- g). optionally, contact the plated areas with an oxidant;
- h). strip away the plating mask;
- i). optionally clean the surfaces of the printed circuit board; and
- 10 j). optionally, coat the resistors with a protective coating.

Steps (a) and (b) together call for the creation of defined circuitry on the surfaces of a metal clad dielectric laminate (or multilayer package - several layers of circuitry containing one or more innerlayers of circuitry which have been

15 laminated into a single planar package. The innerlayers may or may not contain the plated resistors of this invention. If so then the innerlayers may be fabricated by the process described herein). The metal clad laminate may optionally have thru holes in it in a desired array. The thru holes may or may not be plated at this point. The key here is the definition and creation of circuit pattern on the surfaces

20 of the metal clad laminate along with the definition and creation of specific breaks in the circuitry where the resistors will be plated (the "resistor areas"). The length and width of the specific resistor areas will obviously directly impact the resistance achieved after plating.

25 The definition and creation of circuitry and the resistor areas can be accomplished in many ways. The most prevalent way is through the subtractive process as described in current steps (a) and (b). In the subtractive process, a metal (usually copper) clad laminate is used. The metal clad laminate comprises a planar dielectric substrate with metal foil adhered to both exterior surfaces. As discussed,

30 the dielectric substrate is typically glass reinforced epoxy, but can also be a variety of other insulative materials known in the art. In any case a resist pattern is applied

to the metal surfaces such that the resist defines the circuits in a positive manner and the areas between the circuits and the resistor areas in a negative manner. The most typical way of accomplishing this is to use a photoresist. In this case the photoresist is applied to the metal surfaces in either liquid or dry form. The photoresist is then selectively exposed to actinic radiation through a negative. The unexposed areas of the resist are developed away revealing the desired pattern. As an alternative the resist may be screened onto the metal surfaces directly in the desired pattern. After the circuits are defined with the resist, the exposed copper areas are etched away and the resist is stripped revealing the circuits. Thus the areas between the circuits and the resistor areas are now bare dielectric.

Step (c) is optional, but recommended. In order for the resistors to be usable and reliable the resistance must be predictable, relatively constant and reliable. The inventors have found that in order to achieve plated resistors with predictable, relatively constant and reliable resistance, the dielectric surface to be plated with the resistor must be uniform. In this regard the inventors have achieved dielectric surface uniformity and predictable, relatively constant and reliable resistance of the plated resistors by uniformizing the dielectric surface upon which the resistor is to be plated. Uniformizing can be achieved in several ways such as vapor blasting, chemical etching, plasma etching, laser normalization or mechanical uniformization. Mechanical uniformization can be achieved by sanding, sand blasting or shot blasting. The inventors have found that surface uniformization through chemical etching to be the most reliable and efficient means. The particular etchant used in this regard must be matched with the dielectric being used. However, if glass reinforced epoxy is used, the inventors have found that alkaline permanganate, concentrated sulfuric acid, chromic acid or plasma to be particularly useful in etching and uniformizing the surface of the dielectric. Solutions of sodium or potassium permanganate at concentrations in excess of 50 grams/liter, in 10% by weight caustic solution, at temperatures in excess of 140°F and for times of 2 to 20 minutes are preferred in this regard. If permanganates are used in this regard they may be preceded with a swellant or

sensitizer which makes the dielectric more susceptible to the permanganate etch. A typical swellant for epoxy is m-pyrol applied full strength at from 90-120 °F for from 1 to 5 minutes. In addition the permanganate etch is typically followed by an acid reducing solution which will remove the permanganate residues.

5

Step (d) involved activating the surfaces to be plated. Activation of the surfaces can range in complexity from a single dip in a precious metal activator (or non-precious metal or other activators known in the art) to a full plating cycle involving numerous steps. Typically the activation process will begin with a conditioner (surfactant or other type), followed by an activator ($\text{PdCl}_2/\text{SnCl}_2$ Colloid) and an accelerator. Clean water rinses are interposed between each chemical treatment. Regardless of the activation cycle chosen, its primary purpose is to treat the surfaces such that they initiate and accept plating. A wide variety of methods for achieving this are known in the art, any of which may be advantageously utilized here. Please refer to U.S. Patent Nos. 5,032,427 (Kukanskis, et al.), 4,976,990 (Bach et al.) and 4,863,758 (Rhodenizer), the teachings of which are incorporated herein by reference in their entirety.

In step (e) a plating mask is applied such that the resistor areas are defined in a negative manner. Generally, to accomplish this, the plating mask covers all or substantially all of the surfaces except for the resistor areas. The inventors have found that the plated resistors are more reliable if the plating mask allows for some plating overlap where the resistive plating meets the conductive circuit as opposed to covering all of the circuit with plating mask and causing the resistive plating to merely abut the conductive circuit. In any case, the plating mask can be any typical plating mask known in the art as long as it maintains its integrity in the subsequent plating bath. The plating mask may be screened onto the surface in the desired pattern or blanket coated, photoimaged and developed.

Step (f) involves plating the resistors. At this stage the plating will occur only on the areas not covered by the plating mask (i.e. the resistor areas, preferably

with some overlap onto the circuits where the resistor connects to the circuits). A variety of plating baths can be advantageously utilized. The inventors have found electroless nickel-phosphorous, electroless and precious metal plating baths, including palladium-phosphorous, or ruthenium-phosphorous electroless plating
5 baths, to be particularly useful in this regard. It may be optionally desirable to clean and/or accelerate the surfaces prior to plating.

Obviously, the thickness of the metal plated has a direct impact on the resistivity of the resultant resistor. The inventors have found that typically it is
10 advantageous to plate metal thickness in the range of from 0.05 to 2.5 microns, preferably from 0.10 to 1.0 microns and most preferable from 0.10 to 0.50 microns. Plating advantageously takes 2 to 3 minutes, more preferably 5 to 10 minutes depending upon the plating bath used and the ultimate resistance desired.

15 Depending upon the ultimate resistance desired, the following factors may be adjusted to vary the resistivity of the resultant resistor: type of metal plated, thickness of the metal plated, length of the resistor and, width of the resistor. With regard to type of metal plated, the phosphorous content of the nickel-phosphorous or the ruthenium - phosphorous, will affect the resistivity of the final deposit. All
20 of the foregoing factors may be varied to achieve the ultimate resistance desired. The inventors have found that the intrinsic resistance of the nickel or palladium plated increases with the phosphorous content of the metal. They have also found it most advantageous to plate the resistors with nickel having a phosphorous content of 10-13% by weight and palladium with a phosphorous content of 2-8%
25 by weight. The inventors have found that high phosphorous containing metals, particularly nickel or palladium, produce a plated coating with relatively high intrinsic resistance. Therefore, for any given desired ultimate resistance for the resistor, a greater thickness of material (holding length and width constant) can be plated, thereby yielding more reliable plated resistors. This also allows for
30 commercially acceptable plating times in the range of 2-3 minutes. Plating times of less than 2-3 minutes are too short to easily control in a commercial process

with reliability, thereby producing relatively unreliable plated resistors. If resistors of different resistance's are required on the same circuit board, then steps (e) and (f) or (d), (e) and (f) can be repeated to plate different resistors with different thickness of resistive material or with different resistive material. Alternatively, of course, other variables such as length and width of the resistors can be varied without repeating any steps.

Step (g) optionally provides for controlled oxidation of the plated resistor metal preferably by controlled chemical oxidation. The inventors have discovered that controlled oxidation is a method for increasing the resistivity of the plated resistor and more importantly of providing for more predictable resistance on a consistent basis. In this regard a variety of oxidants may be used including potassium iodate, which is preferred. If potassium iodate is used, an aqueous solution with from 10-75 gr/l potassium iodate at a temperature of 90°C and for a time of 5 minutes has proven effective. Have again the higher intrinsic resistance materials allows for greater thickness of plated material (other variables constant), more reliable plated resistors and commercially acceptable plating times. The inventors have found that increases in intrinsic resistance of the plated metal of from 20 to 400 percent based upon the intrinsic resistance of the same unoxidized metal can be achieved.

Step (h) involves stripping away the plating mask. A stripping solution must be chosen to match the plating mask used. Typical plating masks can be stripped away in alkaline solution, however some require organic solvents.

25

At this point, step (i), it is optionally advantageous to clean the surfaces of the printed circuit board in order to remove any residual activator and to increase the surface insulation resistance of the board. U.S. Patent Numbers 5,221,418; 5,207,867; and 4,978,422, the teachings each of which are incorporated herein by reference in their entirety, all teach various means of cleaning and increasing the surface insulation resistance of boards as is suggested by step (i) herein. Care

30

must be taken such that the resistance of the plated resistor is not affected by the foregoing cleaning. It may be advantageous to protect the plated resistors, prior to cleaning the circuit as noted above, through use of a coating of same type, permanent or non-permanent.

5

Finally, it is usually desirable to coat the surfaces of the board, including the plated resistors, with a protective coating such as a soldermask. Soldermask are desirable for the protection of the board in subsequent processing and to enhance the durability of the resulting product. Typical solder mask processing is described in U.S. patent No. 5,296,334, the teachings of which are incorporated herein by reference in their entirety.

Resistivity is the inverse value of conductivity. It is commonly expressed by volume resistivity, surface resistivity and/or insulation resistance as provided for under ASTM D 257. Volume resistivity is the resistance between the faces of a unit cube and is equal to $V=AR/X$ where V is the volume resistivity expressed in ohms-cm, A is the cross sectional area of the electrical path (cm^2), R is the measured resistance (ohms), and X is the length of the electrical path. Values for volume resistivity for the resistors plated as described in this invention can range from about 500 to 1×10^{-4} ohm-cm, and preferably range from about 5 to 5×10^{-4} ohm-cm, most preferably in the range of about 1×10^{-2} to 1×10^{-3} ohm-cm. Surface resistivity is the ability of an insulator to resist the flow of a current in its surface and is equal to $S = PR/d$ where S is the surface resistivity expressed in ohms/square, P is a parameter of the guarded electrode (cm) given in ASTM D 257, R is the measured resistance (ohms) and D is the distance between the electrodes (cm). Insulation resistance is measured on a specific device or configuration and is the integrated effect of volume and surface resistivity. Insulation resistance is usually expressed in ohms and relates to a specific device or configuration. The resistors plated as described in this invention have an insulation resistance which ranges from about 1 to 10,000 ohms, preferably from about 10 to 1,000 ohms.

In applying the foregoing principles to a particular plated resistor with a particular desired design resistance (i.e. insulation resistance) the following equation is useful:

$$R = \frac{VX}{A}$$

where R = the overall desired resistance of the specific plated resistor (i.e. its insulation resistance).

V = volume resistivity of the plated deposit and is generally approximately constant for a particular plating solution.

X = plated resistor length

A = plated resistor cross sectional area (width x thickness)

A typical example may require a plated resistor of 0.005 inches in width, 0.005 inches in length and an overall desired resistance of 275 ohms $\pm$ 15 ohms. Using a plating solution that deposits a modified electroless nickel-phosphorous deposit with a volume resistance of about 7×10^{-3} ohm-cm and depositing a thickness of 10 microinches of the foregoing electroless nickel, a resistor of the desired overall resistance may be obtained as follows:

$$R = \frac{(0.007 \text{ ohm-cm})(0.005 \text{ in})}{5 \times 10^{-8} \text{ in}^2} \times \frac{1 \text{ in}}{2.54 \text{ cm}}$$

$$R = 276 \text{ ohms}$$

If further increases in resistance are required, then the so plated deposit may be oxidized as discussed herein. It should be noted that the key to reproducible results in this regard is surface normalization prior to plating said surface as discussed herein. Post oxidation of the deposit can also increase resistance and improve reproducibility.

30

For comparison purposes, the volume resistivity of plated copper circuitry or copper plated through holes on a printed circuit board is typically less than about

5×10^{-5} ohm-cm and can preferably range from about 1×10^{-6} to 1×10^{-8} ohm-cm. The volume resistivity of the insulative substrate of an FR-4 epoxy-glass printed circuit board is typically greater than about 10^9 ohm-cm and can preferably range from about 10^9 to 10^{20} ohm-cm.

5

With the pace of minaturization of electronic devices, the surface area of printed circuit boards has become more compacted and more valuable. As a result, the overall size of resistors plated in accordance with this invention must fit the size requirement of ever-shrinking printed circuit boards. Plated resistors, prepared in accordance with this invention, with volume resistivity in the range of 500 to 1×10^{-4} ohm-cm can be formed with lengths ranging from about 0.002 in. to 1.0 in., preferably from about 0.005 to 0.20 in., most preferably from about 0.005 to 0.080 in. with widths ranging from about 0.002 to 1.0 in., preferably from about 0.005 to 0.20 in., most preferably from about 0.005 to 0.080 in. and with thickness ranging from about 2 to 300 microinches, preferably from about 5 to 100 microinches and most preferably from about 5 to 25 microinches. Typically, the foregoing length and width dimensions are imaged dimensions (i.e. dimensions of the imaged plating mask in the area to be plated with resistive material). Actual dimensions of the plated resistor may vary somewhat.

20

The following examples are presented for illustrative purposes only and should not be taken as limiting in any way:

25

Example I

Copper clad glass reinforced epoxy laminates were processed through the following sequence:

30

1. A dry film resist (Aquamer CF-1.5 available from MacDermid, Inc.) was laminated to both copper surfaces of the laminate. The resist

was then selectively exposed to ultraviolet light by exposure through a negative. The negative was designed such that the ultraviolet light impinged upon the circuit areas only. (i.e. circuits defined in a positive manner and the areas between circuits and resistor areas are defined in a negative manner) The unexposed portions of the resist were developed away using a 1% by weight potassium carbonate solution at 90°F for 30 seconds.

2. The exposed copper surfaces were etched away by spraying ammoniacal copper chloride etchant at 110°F onto the surfaces until the exposed copper was cleanly etched away. The resist was then stripped away in a 10% by weight caustic solution.

3. The surfaces were activated to accept plating thereon by the following process sequence:

- a). MacDermid M-Conditioner, 110°F, 2 minutes
- b). MacDermid M-Preactivator, 75°F, 2 minutes
- c). MacDermid M-Activator, 100 °F, 5 minutes

Clean water rinses were interspersed between each of the foregoing steps.

4. MacDermid Viatek PM#4 plating mask was then screened onto the surfaces such that it covered all of the surfaces except for the areas where the resistors were to be plated (the "resistor areas") (i.e. such that the resistor areas were defined in a negative manner). The plating mask was then baked to cure for 5 minutes at 250 °F. The width and length of the resistor areas, resistivity of electroless palladium-phosphorous, and the thickness of the palladium-phosphorous plate were used to design and predict the ultimate resistance of the plated resistors.

5. The resistor areas were then plated by immersion in MacDermid Pallas 52 electroless palladium-phosphorous plating bath, which was prepared per the supplied data sheet, at 150 °F for 5 minutes. Approximately 0.1 to 0.2 microns of electroless palladium-phosphorous were plated.

6. The plating mask was then stripped away using a 10% by weight caustic solution at 150 °F for 2 minutes and then thoroughly rinsed.

The boards were then electrically tested to determine the actual resistance of the plated resistors and the actual resistance was compared to the design resistance. Variances of 25-30% were recorded.

Example II

Copper clad glass reinforced epoxy laminates were processed through the same sequence as in Example II except that after step 2 and before step 3 the following additional processing was inserted:

- a). M-Pyrol, 100% by weight, 90°F, 2 minutes
- b). Potassium permanganate, 60 gr/l, 10% by weight caustic soda, 160°F, 10 minutes
- c). 10% by weight hydrochloric acid, 5 gr/l hydroxylamine sulfate, 110°F, 5 minutes.

The boards were then electrically tested to determine the actual resistance of the plated resistors and the actual resistance was compared to the design resistance. Variances of 8-10% were recorded.

Example III

Copper clad glass reinforced epoxy laminates were processed through the same sequence as in Example III except that at the end of the processing as
5 indicated in Example III, the following sequence was performed:

The resistors were oxidized by immersing the boards
in an aqueous solution of 40 gr/l of potassium iodate at
90°C for 5 minutes.

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The boards were then electrically tested to determine the actual resistance of the plated resistors. Actual resistance has increased by 300% as compared to the unoxidized resistors of Example II. Variances of 5 to 10 % were recorded.

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What is claimed is:

1. A method of forming a resistor between two metallic circuit traces, which circuit traces have a volume resistivity less than about 5×10^{-6} ohm-cm, and
5 which circuit traces are upon and separated by an insulative substrate, which insulative substrate has a volume resistivity greater than about 1×10^9 ohm-cm, which method comprises plating a resistive material, which resistive material has a volume resistivity of from about 500 to 1×10^{-4} ohm-cm, onto an area of the insulative substrate between the circuit traces, such
10 that the resistive material connects the circuit traces and wherein the area of the insulative substrate between the circuit traces has been treated with a process selected from the group consisting of chemical etching, plasma etching, laser normalization, vapor blasting, sanding, shot blasting and sand blasting prior to plating the resistive material thereon.
15
2. A method according to claim 1, wherein the insulative substrate is treated by chemical etching prior to the plating of the resistive material.
3. A method according to claim 1, wherein the resistive material is oxidized
20 after being plated.
4. A method according to claim 1, wherein the resistive material comprises a material selected from the group consisting of electroless nickel-phosphorous, electroless palladium-phosphorous, and electroless
25 ruthenium-phosphorous.
5. A method according to claim 2, wherein the resistive material is oxidized after being plated.

6. A method according to claim 2, wherein the resistive material comprises a material selected from the group consisting of electroless nickel-phosphorous, and electroless palladium-phosphorous.
- 5 7. A method according to claim 2, wherein the resistive material is plated to a thickness of from about 2 to 300 microinches.
8. A method according to claim 4, wherein the resistive material is plated to a thickness of from about 2 to 300 microinches.
- 10 9. A process for manufacturing a printed circuit board with integral plated resistors which process comprises:
 - 15 a). applying an etch resist onto portions of the metal surfaces of a metal clad laminate, which laminate comprises a polymer based core with metal cladding thereupon, such that the resist defines the desired circuitry in a positive manner and the areas between the circuits including the locations for the resistors in a negative manner thereby creating exposed metal surfaces and resist covered metal surfaces;
 - 20 b). etching away exposed metal surfaces thereby yielding metal circuits separated by exposed areas of the polymer based core;
 - c). stripping the resist;
 - d). treating at least portions of the exposed areas of the polymer based core with a process selected from the group consisting of chemical etching, plasma etching, laser normalization, vapor blasting, sanding, shot blasting and sand blasting;
 - 25 e). activating at least portions of the exposed areas of the polymer based core to accept plating thereon;
 - f). applying a plating mask such that the plating mask covers all or substantially all of the surfaces of the metal clad laminate except for
30 the locations for the resistors;

- g). plating areas not covered by the plating mask with a resistive material which has a volume resistivity of from about 500 to 1×10^{-4} ohm-cm; and
- h). stripping away the plating mask.

5

10. A process according to claim 9, wherein the resistive material is exposed to an oxidant subsequent to step (g).

10

11. A process according to claim 9, wherein the printed circuit board is cleaned subsequent to step (h).

12. A process according to claim 12, wherein a permanent protective coating is applied to the printed circuit board subsequent to step (h).

15

13. A process according to claim 9, wherein the resistive material is plated to a thickness from about 2 to 300 microinches.

20

14. A process according to claim 9, wherein the resistive material is selected from the group consisting of electroless nickel-phosphorous and electroless palladium phosphorous.

15. A process according to claim 14, wherein the resistive material is plated to a thickness from about 2 to 300 microinches.

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16. A printed circuit board comprising metal circuits upon and separated by a polymer based substrate wherein the metal circuits are connected at specific points by resistive material which has a volume resistivity of from about 500 to 1×10^{-4} ohm-cm, which resistive material has been selectively plated upon the polymer based substrate and wherein at least portions of the polymer based substrate have been treated with a process selected from the

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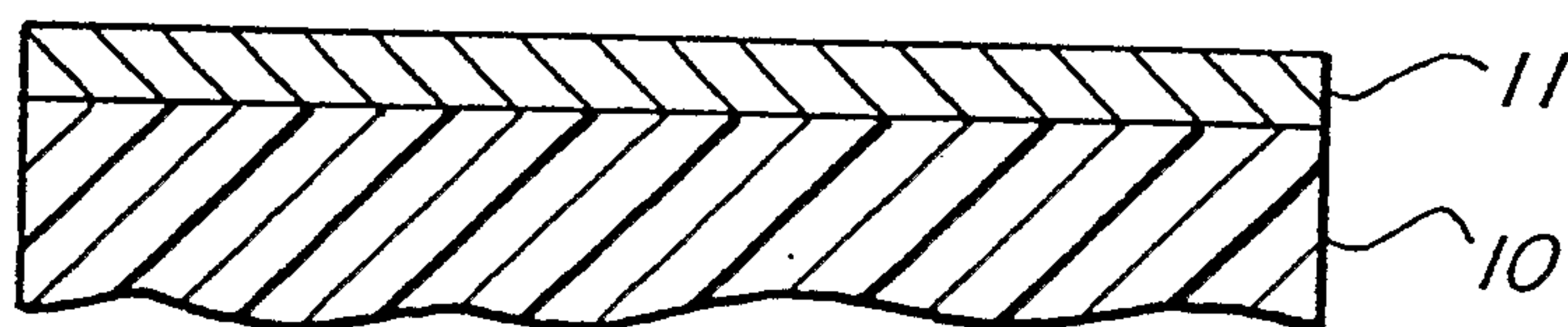
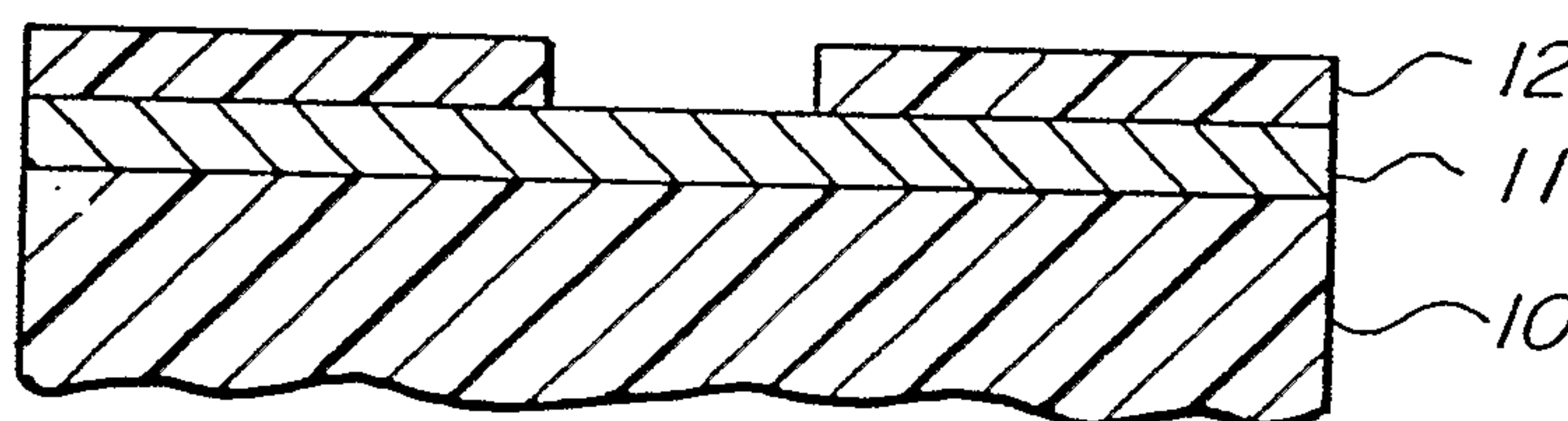
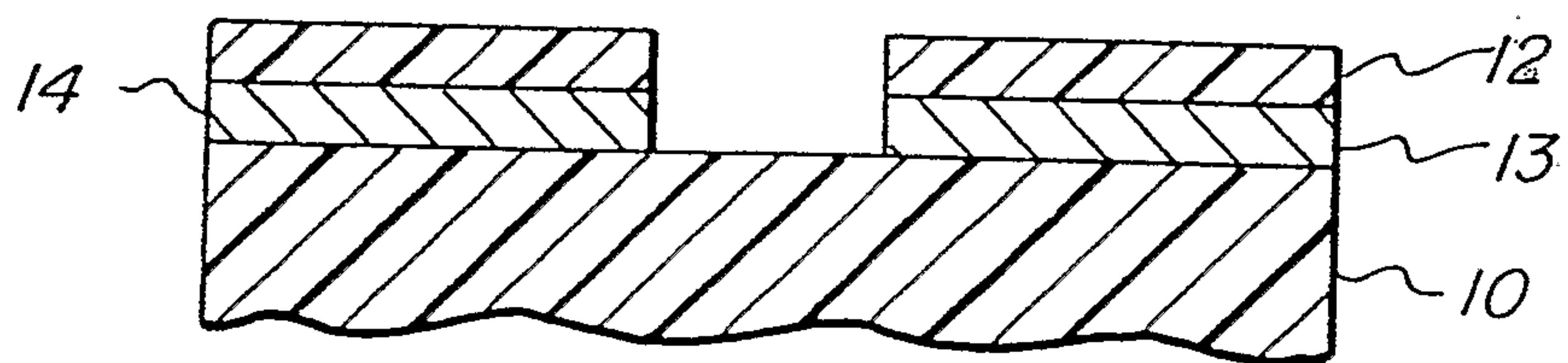
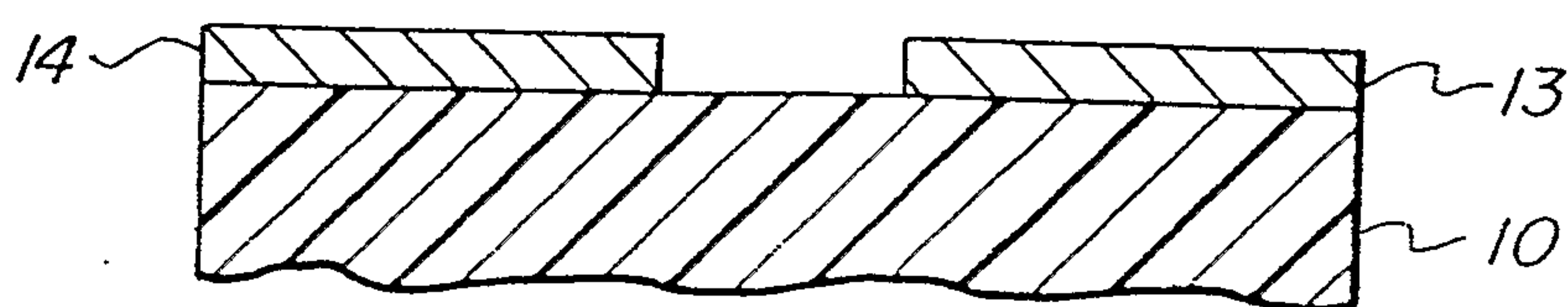
group consisting of chemical etching, plasma etching, laser normalization, vapor blasting, sanding, shot blasting and sand blasting prior to plating the resistive material.

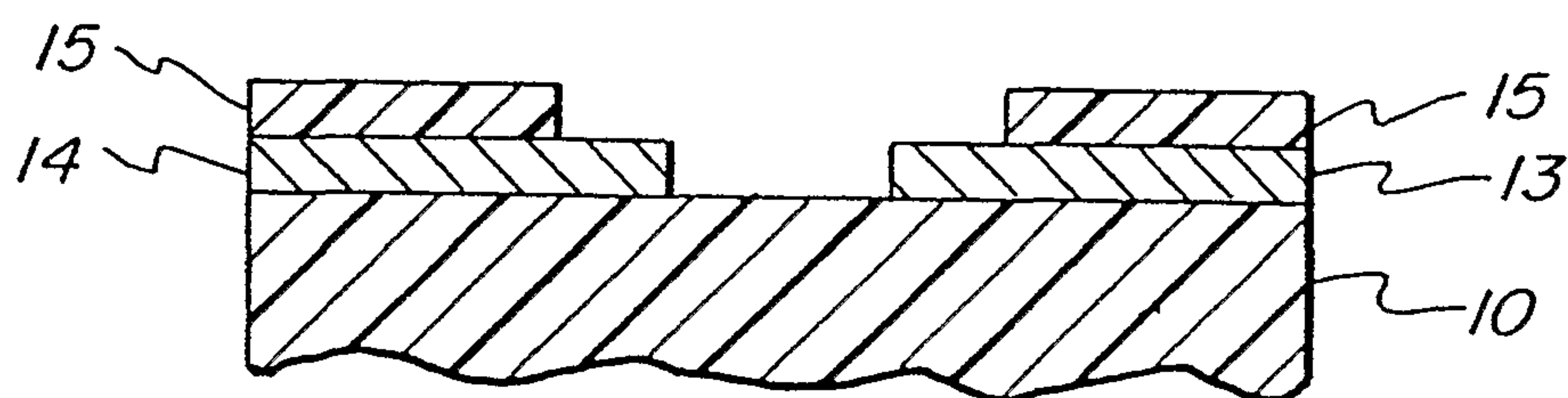
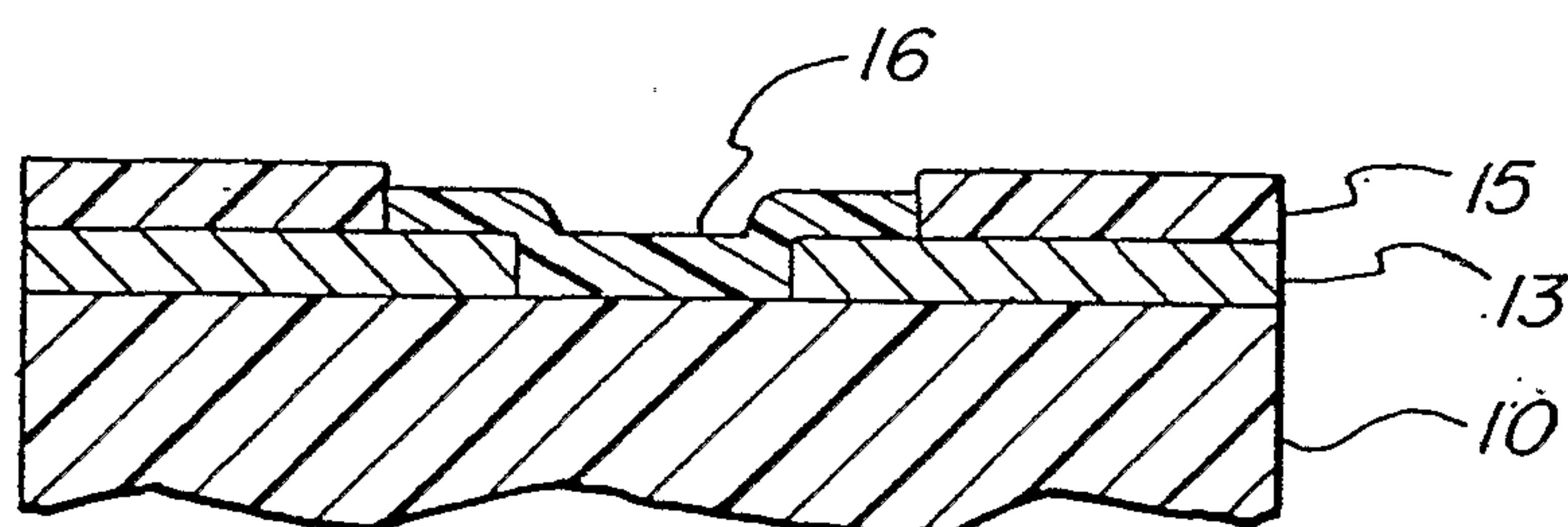
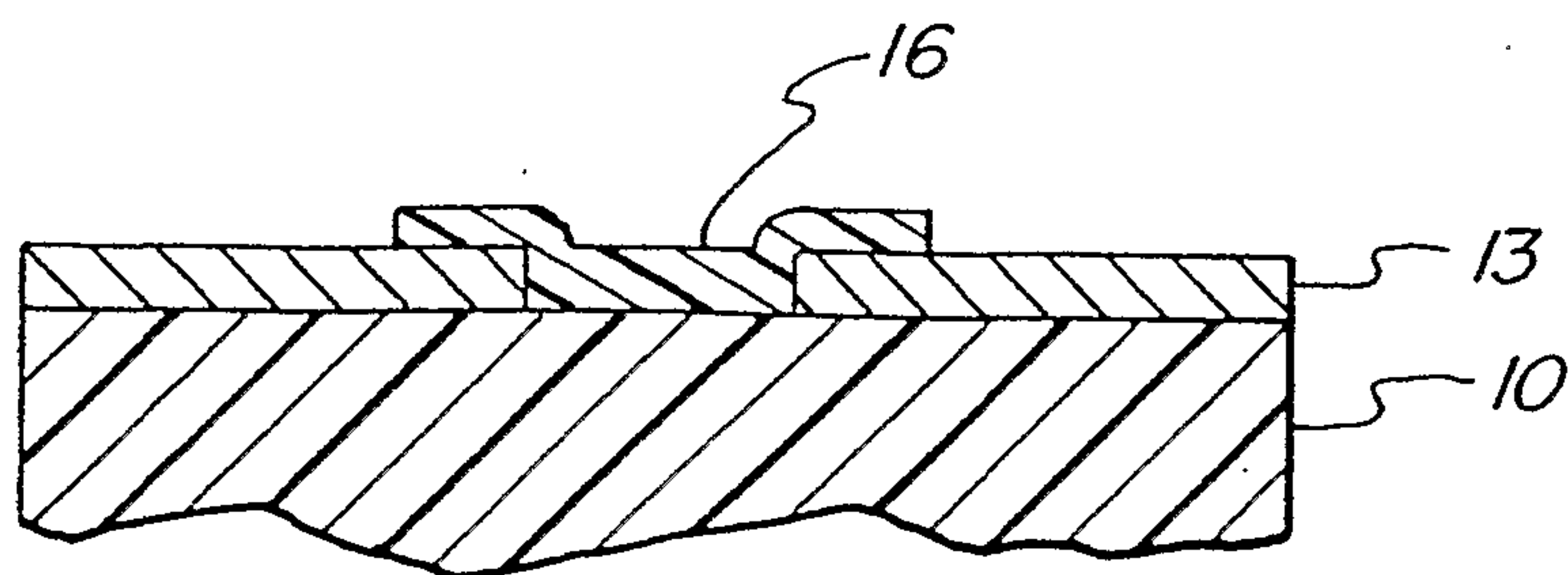
- 5 17. A printed circuit according to claim 23, wherein the resistive material is plated to a thickness of from about 2 to 300 microinches.
18. A printed circuit according to claim 17, wherein the resistive material is selected from the group consisting of electroless nickel-phosphorous, and
10 electroless palladium-phosphorous.
19. A method of forming a resistor between two metallic areas, which metallic areas are upon and separated by an insulative substrate, which insulative substrate has a volume resistivity of from about 10^9 to 10^{20} ohm-cm, and
15 which method comprises plating a resistive material, which resistive material has a volume resistivity of from about 500 to 1×10^{-4} ohm-cm, onto a portion of the insulative substrate which is between metallic areas, such that the resistive material connects the metallic areas and thereafter the plated resistive material is contacted with an oxidant.
- 20 20. A method according to claim 19, wherein the conductive areas are circuits on a printed circuit board.
21. A method according to claim 19, wherein the resistive material comprises a
25 material selected from the group consisting of electroless nickel-phosphorous and electroless palladium-phosphorous.
22. A process for manufacturing a printed circuit board with integral plated resistors which process comprises:

- 5 a.) applying an etch resist onto portions of the metal surfaces of a metal clad laminate, which laminate comprises a polymer based core with metal cladding thereupon, such that the resist defines the desired circuitry in a positive manner and the areas between the circuits, including locations for the resistors, in a negative manner, thereby creating exposed metal surfaces and resist covered metal surfaces;
- 10 b.) etching away the exposed metal surfaces thereby yielding metal circuits separated by exposed areas of the polymer based core;
- c.) stripping the resist;
- d.) treating at least portions of the exposed areas of the polymer based core with a process selected from the group consisting of chemical etching, plasma etching, laser normalization, vapor blasting, sanding, shot blasting and sand blasting;
- 15 e.) activating at least portions of the exposed areas of the polymer based core to accept plating therein;
- f.) applying a plating mask such that the plating mask covers all or substantially all of the metal clad laminate except for locations for the resistors; and
- 20 g.) plating areas not covered by the plating mask with a resistive material to form resistors, wherein the resistors formed have an insulation resistance of from about 10 to 1000 ohms, a length of from about 0.005 inches to 0.20 inches, a width of from about 0.005 inches to 0.20 inches and a thickness of from about 5 to 100 microinches.
- 25

23. A process according to claim 22, wherein the resistor is exposed to an oxidant subsequent to step (g).

24. A process according to claim 22, wherein the printed circuit board is cleaned subsequent to step (g).
25. A process according to claim 22, wherein the resistive material is selected
5 from the group consisting of electroless nickel-phosphorous and electroless palladium-phosphorous.
26. A process according to claim 22, wherein a permanent protective coating is applied to the printed circuit board subsequent to step (g).
- 10 27. A process according to claim 22, wherein the resistors overlap onto the metal circuits.
28. A process according to claim 22, wherein the resistors have a length of
15 from about 0.005 to 0.080 inches, a width of from about 0.005 to 0.080 inches and a thickness of from about 5 to 25 microinches.

*FIG. 1A**FIG. 1B**FIG. 1C**FIG. 1D*

*FIG. 1E**FIG. 1F**FIG. 1G*

