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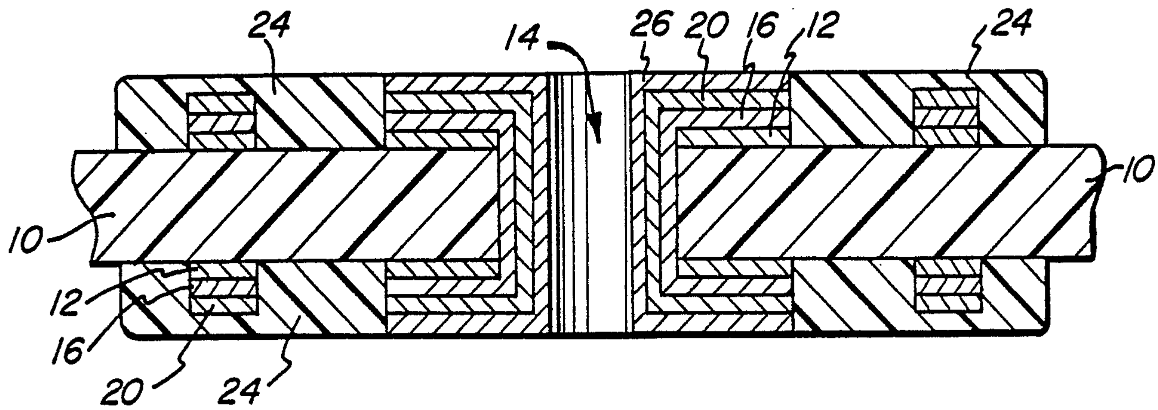

(57) Abstract

A method of preparing printed circuit boards in which the solder mask (24) is applied over a thin layer ("smut") of tin covering the copper circuit traces, the tin layer being that which remains after stripping tin or tin-lead alloy etch resist (22). This represents a significant cost saving as compared with processes in which the tin-lead alloy (20) is completely stripped leaving bare copper to which the solder mask (24) is applied in the SMOBC type of circuit board.

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METHOD FOR MANUFACTURE OF PRINTED CIRCUIT BOARDS

BACKGROUND OF THE INVENTION

The present invention relates to printed circuit boards of the type having a solder mask over non-reflowable metal and, more particularly, to a method of manufacture of such circuit boards and to the unique printed circuit boards resulting therefrom.

As is well understood in the art, the manufacture of double-sided printed circuit boards requires the provision of conductive through-holes for interconnecting components on opposite sides of the board or, in the case of multilayer printed circuit boards, for interconnecting the inner layers. The nonconductive surfaces exposed when through-holes are drilled in a non-conductive substrate having metal cladding on both sides must, therefore, be provided with a conductive coating, and this generally is accomplished by a first electroless deposition of copper onto the suitably conditioned through-hole surfaces, followed by electroplating of copper to build up additional thickness.

In application of the actual circuit patterns to the metal-clad board surfaces, it is necessary to employ plating resists so as to prevent all but particular areas of the board (through-holes and/or traces and/or pads and/or other areas) from receiving applied metal platings such as the copper electroplate used in through-hole plating or the commonly-employed tin-lead coating applied as an etch-resist preliminary to the step of etching away undesired metal down to the non-conductive substrate surface so as to form the appropriate conductive circuit pattern.

Apart from its use as an etch-resist, tin-lead is a preferred overplating for otherwise exposed copper areas on the circuit board so as to prevent oxidative degradation of the copper surfaces and to ensure subsequent soldering of components.

In the ultimate fabrication of a printed circuit board in which various components and connections are soldered, it is generally accepted that improved solderability of circuit pads and through-holes can be provided to the ultimate fabricator by having the manufacturer precoat these areas with a solderable metal, generally a tin-lead composite closely similar in composition to the solder actually used in the eventual soldering of components and connections. For applications where hand-soldering by the fabricator is to be performed, little difficulty is encountered in applying solder to desired areas without disturbing or inadvertently soldering adjacent conductive traces. However, when soldering is to be conducted in mass techniques, such as with wave soldering or dip soldering methods, inadvertent soldering and improper connections can occur. As a consequence, manufacturers apply a solder resist or solder mask over those areas of the board to be protected from solder, including the tin-lead coated copper traces.

It has been recognized that the technique of solder resist over tin-lead coated copper can, however, lead to its own peculiar problems. For example, since the tin-lead is a reflowable metal, ultimate wave or dip soldering can cause the tin-lead to wick up under the mask or simply to melt and no longer provide support for the mask. Due to these disadvantages, it has been proposed to apply the solder mask directly over bare copper at those areas where protection from solder is desired. This "solder mask over bare copper" (SMOBC) technique avoids the problems inherent in the application of the mask over tin-lead coated copper, and can yield printed circuit boards with finer line definition and higher circuit density capabilities. Unfortunately, the known solder mask over bare copper techniques involve added manufacturing operations, and hence added cost, and present waste disposal and pollution control problems.

In order to explain these disadvantages in more detail, a typical SMOBC process is schematically set forth in the cross-sections represented by FIGS. 1A through 1J. Layer thicknesses and through-hole sizes are not representative of either actual or relative scale. For ease of representation of the various steps in the process, a section of the printed circuit board is shown involving, on each side, one through-hole, one pad, and one trace line; the trace will be in association with a different pad and through-hole area on the board (not shown), while the through-hole and pad will be associated with a different trace on the board (not shown).

As shown in FIG. 1A, a non-conductive substrate 10, typically an epoxy glass resin, has applied to it on both sides thin copper foil laminate 12. A through-hole 14 has been drilled in the laminated board, and the inner hole surfaces are thus composed of the non-conductive substrate.

In order to provide a conductive connection between the circuitry eventually applied on both sides of the laminate, the through-hole surfaces must be made conductive. As shown in FIG. 1B, the first step in this process is to electrolessly deposit a copper layer 16 on the entirety of the board, i.e., on the through-hole surfaces and on the copper foil 12 (conditioning and activating steps preliminary to copper deposition not shown).

The desired circuit pattern is then applied to the electroless copper layer through application and subsequent exposure and development of a negative photoresist. The areas of the photoresist exposed to light cross-link and become insoluble to developers which remove non-exposed, non-cross-linked areas. As a consequence, there are now present on the electroless copper layer, exposed copper areas corresponding to traces, pads and through-holes, while remaining areas are covered by material 18 resistant to subsequent plating, as shown in FIG. 1C.

In the next step in the process, copper thickness in the exposed areas is built up through an electroplated copper layer 20 to arrive at the configuration shown in FIG. 1D.

Following copper electroplating, an etch resist 22, generally tin-lead, is electroplated onto exposed copper surfaces as depicted in FIG. 1E. After completion of this step, the plating resist 18 is removed (FIG. 1F) in preparation for copper etching, the etching resulting in the configuration shown in FIG. 1G.

Since the solder mask is to be applied to bare copper, the tin-lead etch resist 22 is stripped away in the next step as shown in FIG. 1H. It is now desired to solder coat the pads and through-holes but not the traces and, accordingly, a solder mask 24 is applied to the board in a pattern appropriate to protect all areas where solder is undesired, as shown in FIG. 1I. Thereafter, the exposed copper at the holes and pads is cleaned and prepared for solder coating, and then solder coated by, e.g., immersion in a solder bath followed by hot air level solder to present the solder-coated surface 26 as shown in FIG. 1J. Electrolytic processes for application of a solder coat cannot be employed in this method at this stage since the prior step of copper etching has removed the electrical continuity among areas of the board.

As will be readily apparent, the known techniques for solder mask over bare copper, while effective for eliminating problems inherent in application of solder mask to tin-lead coated copper, involve a number of steps which on their face appear almost duplicative but which nevertheless are necessary to gain the advantages of SMOBC. In particular, it will be seen that tin-lead is applied in the normal course of manufacture as an etch-resist over surfaces such as traces, pads and holes, and this tin-lead etch-resist is generally of the same or similar alloy composition as the solder eventually applied to the pads and holes. Nevertheless, the manufacturing sequence requires that this tin-lead etch-resist be stripped and removed so that effective solder masking of bare copper traces can be accomplished. Not only do these additional steps result in increased manufacturing cost, but significant waste removal and pollution concerns arise.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide printed circuit boards of the type in which a solder mask is present directly over a non-reflowable metal coated on bare copper surfaces.

A further object of the invention is to provide a process for manufacturing boards of the type described which is economical in execution and eliminates problems present in known processes as to waste disposal.

A more particular object of the invention is to provide printed circuit boards, and methods for their manufacture, of the type containing solder-coated pads and through-holes, and solder mask applied directly over a non-reflowable metal coated on bare copper surfaces.

The term "non-reflowable metal" as used herein means a metal which does not flow at any of the temperatures employed in the processing steps involved in the preparation of the printed circuit board when said metal is in place on said board.

The above objects, and other objects which will become apparent from the description which follows, are achieved by the process of the invention wherein the process of stripping the tin-lead etch resist prior to application of the solder-mask is not carried to completion, i.e., to the stage at which bare copper surface is exposed, but is terminated when a thin film of tin residue remains on the copper surface. This residue (hereinafter "tin smut") is principally tin but may also contain small amounts of other components such as residual lead and or metal oxides. Thereafter the solder mask is applied selectively to the board including the trace surfaces covered by the thin film of tin smut but not the loci which are to receive solder such as the throughholes, surrounding pad surfaces and any lands for attachment of surface mount devices (SMD's) and the like which may be present. As will be appreciated by one skilled in the art, there may be other areas or devices present on the board such as fingers and the like which are not to receive either solder mask or solder. In the interest of brevity, it will be assumed for purposes of the description which follows that, if such areas or devices are present, the appropriate steps conventionally employed in the art will be taken to prevent deposition of unwanted solder mask or solder at these locations whether or not such steps are specifically mentioned.

After the solder mask has been applied the thin layer of tin smut remaining exposed on the surface of the copper at the loci to which solder is to be applied is removed using an appropriate tin stripper typlically an acid. The bare copper surfaces so exposed are then subjected to a soldering step to yield the finished circuit board.

The method of the invention eliminates the need for complete removal of etch resist from all trace surfaces, which process is frequently accompanied by loss of copper from the underlying copper layer due to the vigorous stripping conditions such as those encountered using strong oxidizing acids. The principal type of stripper composition employed to remove such tin-lead etch resists is based on a combination of a nitrosubstituted aromatic compound such as nitro-substituted aromatic sulfonic acids and salts thereof and an acid such as fluoboric, acetic or like aliphatic acids or aromatic acids. The nitro-aromatic compounds are oxidants for the tin-lead and the other acid is an acceptor for the cations so oxidized. Illustrative of such compositions are those disclosed in U.S. Patents 3,677,949; 4,004,956; 4,397,153; and 4,439,338.

Another type of stripper employed to remove tin-lead etch resists is based on hydrogen peroxide as the principal active ingredient in acidic medium. Representative of this type of composition are those disclosed in U.S. Patents 3,926,699; 3,990,982; 4,297,257; 4,306,933;

4,374,744 and 4,424,097. However such compositions have a number of disadvantages. Thus, they are too unstable on storage to be provided in ready-to-use form and have to be prepared just prior to use. Further the reaction involved in the stripping using the hydrogen peroxide based compositions is highly exothermic and the tin-lead alloy turns black. A white deposit is formed on the substrate and significant attack and removal of copper from the substrate takes place.

The nitro-aromatic compound-based compositions discussed above are generally preferred because they are reasonably stable and are less aggressive towards the copper substrate than the hydrogen peroxide based compositions. However they normally leave a residual thin layer of tin ("tin smut") thought to be due to redeposition of tin from the stripping bath or incomplete stripping. Such redeposition of tin can be avoided by replacing the stripping bath at frequent intervals to prevent build up of tin therein but this adds greatly to the processing costs and is therefore undesirable.

It has now been found that it is unnecessary to remove the aforesaid tin smut layer from the underlying copper before applying the solder mask to the circuit trace patterns. This finding not only significantly reduces the time and cost normally involved in removing this residual film of tin smut in order to expose the underlying copper but is highly unexpected in that the overall performance of the final circuit board is not affected deleteriously. The present invention therefore takes advantage of what has hitherto been regarded as a drawback in the process of the prior art, namely, the production of a residual tin smut film which was difficult to remove in the final stages of stripping the etch resist. The invention also goes counter to conventional wisdom which has considered it to be desirable, if not essential, to remove all traces of the etch resist before applying the solder mask.

The process of the invention has been discussed above in regard to the use of tin-lead alloy as etch resist. The process of the invention can also be applied where tin rather than tin-lead alloy is employed as etch resist. The use of tin etch resist rather than tin-lead etch resist has the advantage of avoiding the need to dispose of waste products containing lead. The steps of the process of the invention are exactly the same whether the etch resist is tin or tin-lead alloy and it is to be understood that the invention is not limited to the use of tin-lead alone. However, in the interests of brevity, the further description will be directed to illustrating the invention as it applies to processes employing tin-lead as etch resist.

As will be readily apparent to one skilled in the art, the process of the invention is applicable not only to the manufacture of double sided printed circuit boards as discussed above but also to other types of printed circuit boards including single sided boards, semi-additive type boards, molded boards, multilayer boards and the like. The invention will be illustrated hereinbelow by reference to the manufacture of double sided printed circuit boards but this is for purposes of illustration only and the scope of the present invention is not limited thereto.

BRIEF DESCRIPTION OF THE DRAWINGS

As previously noted, FIGS. 1A through 1J represent schematic illustrations of a circuit board cross-section during its various stages in a known solder mask over bare copper (SMOBC) manufacturing method.

DETAILED DESCRIPTION OF THE INVENTION

The method of the invention is carried out broadly in accordance with procedures and using materials conventionally employed in the art to fabricate printed circuit boards but with the exceptions that (i) the stripping of the tin-lead alloy etch resist is not carried to completion but is terminated when a thin film of tin remains on the surface of the underlying copper circuit traces and through-holes and surrounding pads (ii) the solder mask is applied to circuit board including the copper circuit traces covered with tin smut but not over the tin smut layer on the loci which are to receive solder and (iii) the tin layer on the latter locations is subsequently removed prior to the application of solder to the underlying copper at those locations.

Thus, the method of the invention makes use of a conventional non-conductive substrate, containing through-holes and having a layer of copper such as copper foil laminated on both sides of the substrate, generally in an amount to provide a coverage of about one ounce of copper per square foot (0.0014 inches thickness) on each side. The copper surfaces and the exposed non-conductive through-hole surfaces are then treated according to any known electroless copper depositing process (including the various conditioning, activating, accelerating, and rinsing steps involved in conditioning the surfaces and securing suitable deposition) to deposit a layer of copper thereon, generally of about 40 to 120 X 10^{-6} inches in thickness.

A plating resist which can be any of those conventionally employed in the art, is then applied to the electroless copper surfaces. Such plating resists include inks which can be applied in the required pattern by stencil or screen printing or other known methods. Generally, the resist will be a photosensitive type (negative or positive-acting) and can be of the dry film or liquid type. Dry film resists will be employed where it is desired that certain through-holes receive no further coatings, since the dry film will easily tent over and protect these holes. Alternatively, these holes can be plugged with liquid resists. Preferably the plating resist will be a negative photoresist in which exposure to light results in insolubilizing of the resist material, while those areas not exposed to light remain in a form which permits dissolution and removal with a suitable developer. The through-holes and surrounding pads, and any other loci, such as lands for attachments of SMD's and the like, which are to receive solder, are not protected with plating resist material. An electroplated copper coating is applied to these loci as well as to the pattern traces created in the plating resist. Any of the known plating techniques and baths can be employed.

A tin-lead alloy etch resist is then applied, advantageously by known electroplating techniques, to the pattern traces and all exposed copper surfaces after which the plating resist is removed using techniques well-known in the art. The copper layers which had been covered by the plating resist are then etched away using standard techniques and using appropriate copper etchants to which the etch resist tin-lead coating is resistant.

It is the next step of the process wherein the present invention first departs from the conventionally employed procedures for fabricating printed circuit boards. Thus, instead of removing the tin-lead alloy etch resist completely using strong oxidizing acids and exposing bare copper in the circuit traces, through-holes and pads, the stripping is carried out under conditions such that a thin layer of tin smut remains on the surfaces in question due to redeposition of tin from the stripping bath. This step is conveniently accomplished by immersing the substrate in a bath of the stripper composition advantageously at a temperature of about 20°C to about 70°C and preferably at a temperature of about 25°C to about 60°C.

The stripper composition employed in the above step is preferably one which comprises as the main active ingredients, a nitro-substituted aromatic compound and an inorganic or organic acid or acids. The nitro-substituted aromatic compound can be any aromatic compound having one or more nitro-substituents on the aromatic ring and having a water-solubilizing substituent also attached to the aromatic ring. Illustrative of such compounds are o-, m- and p-nitrobenzene sulfonic acids and alkali metal salts thereof; o-, m- and p-nitrobenzoic acids and alkali metal salts thereof; o-, m- and p-nitrochloro benzenes, o-, m- and p-nitrophenols; and o-, m- and p-nitroanilines and mineral acid salts thereof. A preferred group of nitro-substituted aromatic compounds are the nitrobenzene sulfonic acids and alkali metal salts thereof. A particularly preferred such compound is sodium m-nitrobenzene sulfonate.

The acids employed in association with the nitro-aromatic compounds can be any of those which are capable of readily reacting with tin and lead to form water-soluble salts but which do not form a water-insoluble film on the tin or tin-lead alloy being stripped. Illustrative of such acids are fluoboric and fluosilicic acids and sulfamic acid.

Optionally, but preferably, there is also present in the above stripper compositions an organic acid such as formic, acetic, propionic, chloroacetic, bromoacetic, trichloroacetic acids and the like which act as accelerators in enhancing the rate of stripping.

The various components of the stripping composition are present advantageously in proportions within the following ranges:

nitroaromatic compound:	30 to 120 g. per liter
inorganic acid:	50 to 200 g. per liter
organic acid:	25 to 100 g. per liter
water:	to make 1 liter.

When the above stripping step has been completed the circuit board is rinsed with water and dried. Thereafter a layer of solder mask is applied selectively over the whole board including the tin-coated copper circuit traces but not over the loci which are to receive solder. Any of the known solder masks can be used and applied in accordance with standard techniques such as screen printing and the like. The application of the solder mask over the tin layer represents the second significant departure from the prior art procedures.

In the penultimate step of the invention, the tin smut layer remaining over the copper layer at the loci to receive solder is removed to expose bare copper at those locations. This is accomplished by subjecting the circuit board to the action of any of the strong oxidizing acid stripper compositions conventionally employed to remove traces of tin from copper. A particularly preferred stripper composition is an aqueous solution of a mixture of nitric and fluoboric acids. Illustratively such a solution contains equal parts by weight of the two acids in about 2 parts by weight of water per part by weight of total acid.

The stripping of the tin smut layer is accomplished conveniently by immersing the substrate in a bath of said stripper composition. The latter is preferably at a temperature within the range of about 20°C. to about 70°C. and most preferably at a temperature within the range of about 25°C to about 60°C. The progress of the removal of the smut-layer of tin can be followed best by visual inspection the endpoint being signalled by a change in color of the surface of the substrate from the brown-gray of the tin smut-film to the bright color of clean copper. When this stage is reached, generally within a matter of a few minutes, the substrate is removed from the bath and rinsed with water to remove last traces of the stripper solution.

In an optional step the clean copper surface so produced is coated with an organic protective coating such as that available under the trade name SEALBRITE from London Chemical Company to protect the copper layer from oxidation by contact with air prior to the soldering step. In the latter step the solder can be applied directly over the coating without removing the latter.

The final step of the method of the invention comprises applying solder to the clean copper surfaces or to said surfaces protected by SEALBRITE using conventional techniques such as by immersion in a solder bath followed by the known hot air levelling procedure.

In a modification of the embodiment set forth above the penultimate step of the process, namely, the stripping of the tin smut layer from the loci which are to receive solder, is carried out using an aqueous solution containing a mixture of an alkali metal hydroxide and an alkali metal chlorite. Any of the alkali metal hydroxides and chlorites, i.e. the sodium, potassium and lithium hydroxides and chlorites can be used in any combination. However, a particularly preferred combination comprises a mixture of sodium hydroxide and sodium chlorite. The alkali metal hydroxide is advantageously employed in a concentration within the range of about 10 to about 200 grams per liter and, preferably, in the range of about 100 to about 200 grams per liter. The alkali metal chlorite is advantageously employed in a concentration within the range of about 5 grams per liter up to saturation and, preferably, in the range of about 50 to about 150 grams per liter. The stripping using the above composition is accomplished conveniently by immersing the substrate in a bath of the composition. The latter is preferably heated or pre-heated to a temperature within the range of about 20°C. to about 100°C. and most preferably to a temperature within the range of about 50°C. to about 100°C. The progress of the removal of the smut-layer of tin can be followed best by visual inspection. The endpoint is signalled by a change in color of the surface of the substrate from the brown-gray of the tin smut-film to a dark brown or black color due to formation of a film of copper oxide. When this stage is reached, generally within a matter of a few minutes, the substrate is removed from the bath and rinsed with water to remove last traces of the stripper solution.

The layer of copper oxide which remains on the copper layer at the through-holes and surrounding pads is then removed by immersing the circuit board briefly in a bath of aqueous acid such as dilute sulfuric or hydrochloric acids for a time sufficient to effect removal of the copper oxide. The final step of the process, namely, application of solder, is then carried out as described in the embodiment discussed previously.

The use of this modified penultimate step in the process of the invention has the advantage that it employs a less aggressive stripping of tin smut from the areas to receive solder than that employed in the other embodiment. There is thus less likelihood of loss of any significant amount of copper from the underlying copper layer at the locations in question.

The procedure of the invention, in addition to the advantages of reduced costs and time of operation, possesses a number of other benefits which will be apparent to one skilled in the art. Illustratively, if there is to be any significant interval of time between the step of applying the solder mask and the step of applying solder to the through-holes and pads, the circuit board can be stored after application of the solder mask and the thin layer of tin on the through-holes and pads is removed immediately before applying the solder. In this way the oxidation of copper surface, which would occur if the tin coatings were removed and the resulting circuit board stored before application of the solder, is avoided very neatly. Other such benefits will be readily apparent to one skilled in the art.

WHAT IS CLAIMED IS:

1. A method for manufacturing printed circuit boards said method comprising the steps of:

(a) providing a non-conductive substrate having a copper layer on both sides thereof and having through-holes made therein;

(b) electrolessly depositing copper on the copper layer and through-hole and surrounding pad surfaces;

(c) applying a resist image of a trace pattern on said copper layer;

(d) subjecting the resulting substrate to a copper electroplating process to deposit additional copper thickness on all exposed copper surfaces including said trace pattern and said through-hole and surrounding pad surfaces;

(e) applying a tin or tin-lead alloy etch resist to said exposed copper surfaces;

(f) removing the imaged material;

(g) removing all copper from those areas not protected by said etch resist;

(h) subjecting said etch resist to the action of a stripper composition comprising an oxidant for the metals of said resist and an acceptor for the cations so oxidized to leave a thin film of tin smut on said surfaces previously protected by said etch resist; and

(i) selectively applying a solder mask to at least the said trace pattern.

2. A method according to Claim 1 which comprises the additional steps of:

(j) removing said thin film of tin smut from the loci which are to receive solder; and

(k) applying solder to said loci.

3. A process according to Claim 1 wherein said stripper composition comprises an aqueous solution comprising fluoboric acid and a member selected from nitro-substituted aromatic sulfonic acids and alkali metal salts thereof.

4. A process according to Claim 3 wherein said nitro-substituted aromatic sulfonic acid is m-nitrobenzene sulfonic acid and said stripper composition also comprises acetic acid.

5. A process according to Claim 2 wherein said step (j) is accomplished by dipping in a bath of an aqueous acid.

6. A process according to Claim 5 wherein said acid bath comprises an aqueous solution comprising a mixture of nitric and fluoboric acids.

7. In a method for manufacturing printed circuit boards the steps comprising:

(a) providing a circuit board material containing through-holes and pads surrounding the surface openings of said through-holes, said board comprising a non-conductive substrate material having copper foil laminated to each side thereof, the areas defined by said through-holes comprising layered coatings, radially inward to the center of said hole, of electroless copper, electroplated copper and etch resistant electroplated tin-lead, the areas defined by said pads comprising layered coatings, commencing from said non-conductive substrate surface, of electroless copper, electroplated copper and etch resistant electroplated tin-lead, and having a trace pattern on at least one surface of said non-conductive substrate comprising layered coatings, commencing from said substrate surface, of copper foil, electroless copper, electroplated copper and etch resistant electroplated tin-lead;

(b) removing copper from the areas of said circuit board not provided with said etch resistant tin-lead layer;

(c) subjecting said tin-lead etch resist to the action of a stripper composition comprising an oxidant for the metals of said resist and an acceptor for the cations so oxidized until a thin film of tin smut remains on said trace pattern, through-holes and surrounding pad surfaces;

(d) selectively applying a solder mask to the said trace pattern but not to said through-holes, surrounding pad surfaces and any other loci which are to receive solder;

(e) removing said thin film of tin smut from said loci which are to receive solder; and

(f) applying solder to said loci.

8. A process according to Claim 7 wherein said stripper composition comprises an aqueous solution comprising fluoboric acid and a member selected from nitro-substituted aromatic sulfonic acids and alkali metal salts thereof.

9. A process according to Claim 8 wherein said nitro-substituted aromatic sulfonic acid is m-nitrobenzene sulfonic acid and said first stripper composition also comprises acetic acid.

10. A process according to Claim 7 wherein said step (e) is accomplished by dipping in a bath of aqueous acid.

11. A process according to Claim 10 wherein said acid bath comprises an aqueous solution comprising a mixture of nitric and fluoboric acids.

12. A process according to Claim 7 wherein said step (e) is accomplished by immersion in a bath comprising an aqueous stripper solution of a mixture of an alkali metal

hydroxide and an alkali metal chlorite thereby removing said tin smut layer from said loci which are to receive solder and producing thereon a layer of copper oxide which layer is removed using aqueous acid before step (f) is carried out.

13. A process according to Claim 12 wherein said aqueous stipper solution comprises a mixture of sodium hydroxide and sodium chlorite.

14. In a process for the preparation of a circuit board which includes the steps of employing tin or a tin-lead alloy as etch resist during the etching of unwanted copper, subsequently stripping said tin or tin-lead alloy and applying solder mask to the copper circuit pattern, the improvement which comprises:

(a) subjecting the tin or tin-lead alloy resist to the action of a stripper composition comprising an oxidant for the metals of said resist and an acceptor for the cations so oxidized until a thin film of tin smut remains on the copper substrate; and

(b) applying solder mask directly over the tin smut layer on the copper circuit pattern.

15. A process according to Claim 14 wherein said stripper composition comprises an aqueous solution comprising fluoboric acid and a member selected from nitro-substituted aromatic sulfonic acids and alkali metal salts thereof.

16. A process according to Claim 15 wherein said nitro-substituted aromatic sulfonic acid is m-nitrobenzene sulfonic acid and said stripper composition also comprises acetic acid.

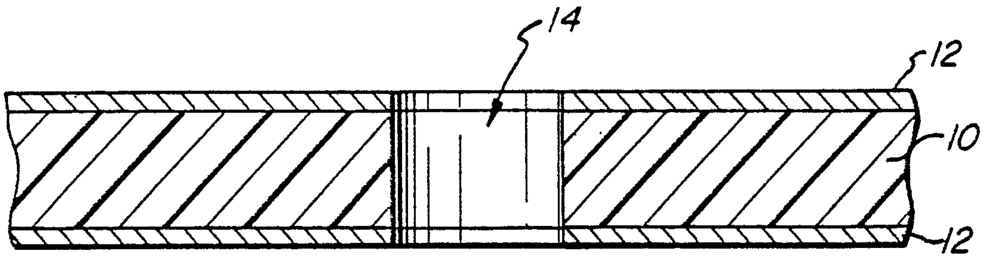

FIG. 1A

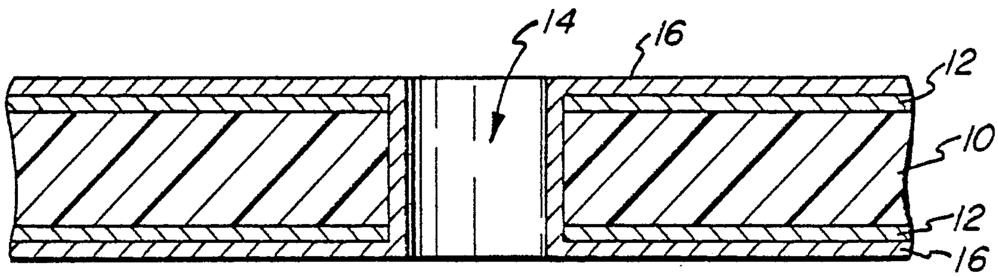

FIG. 1B

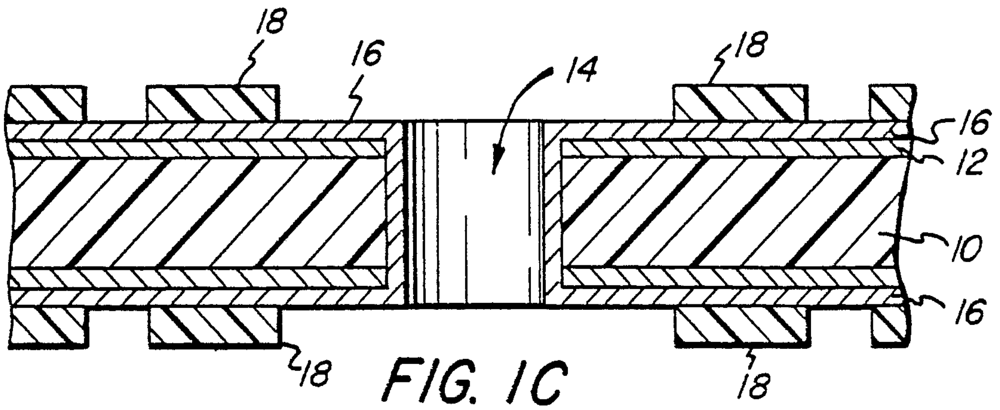

FIG. 1C

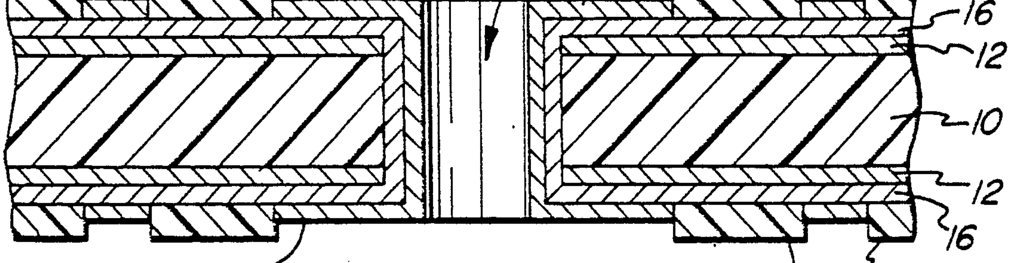

FIG. 1D

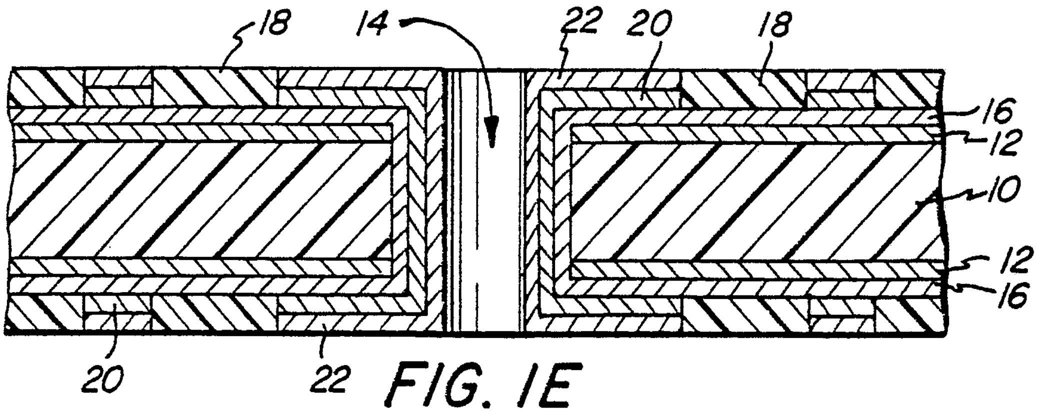

FIG. 1E

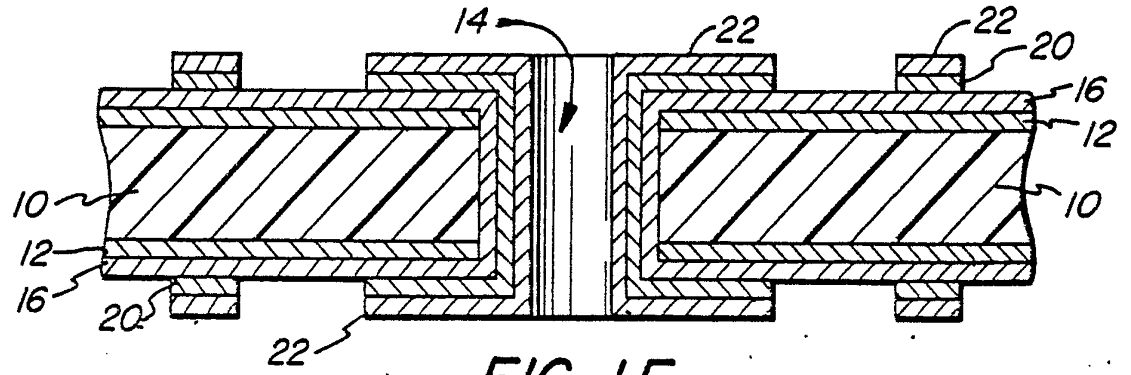

FIG. 1F

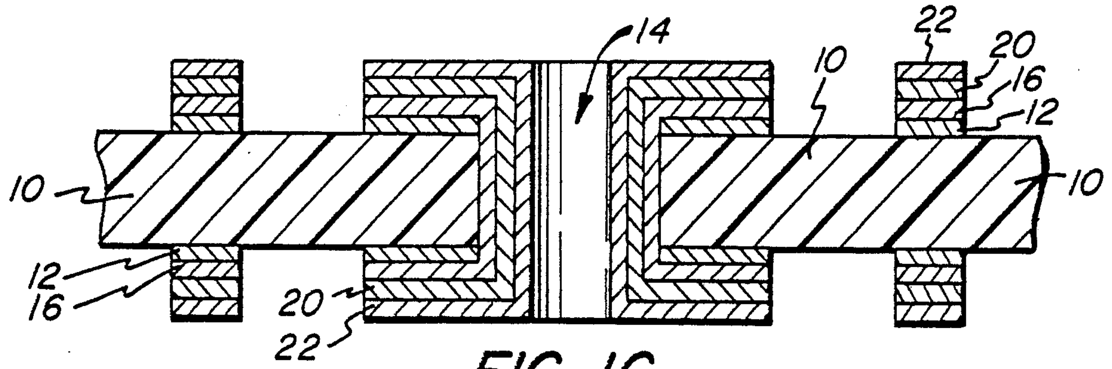

FIG. 1G

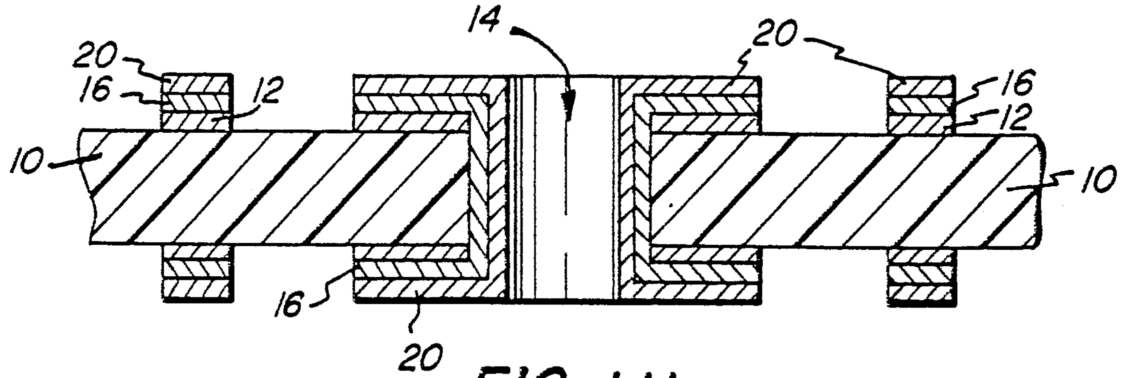

FIG. 1H

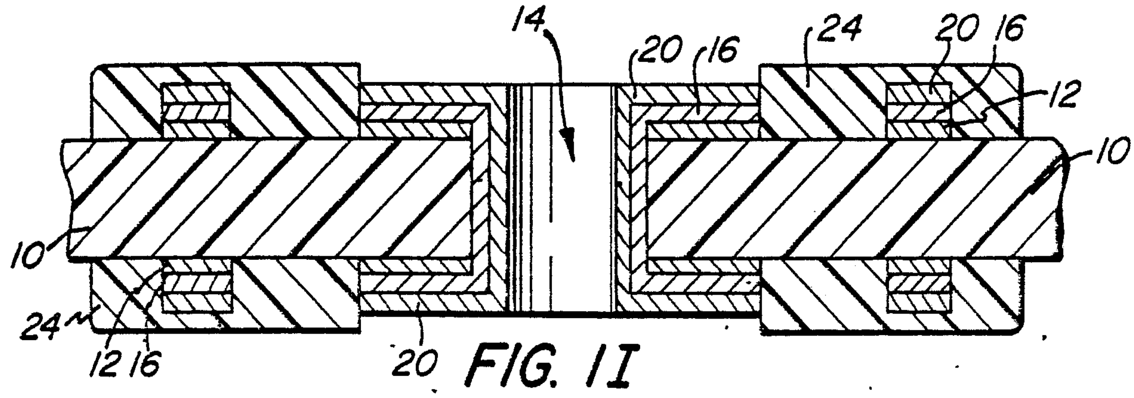
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FIG. 1I

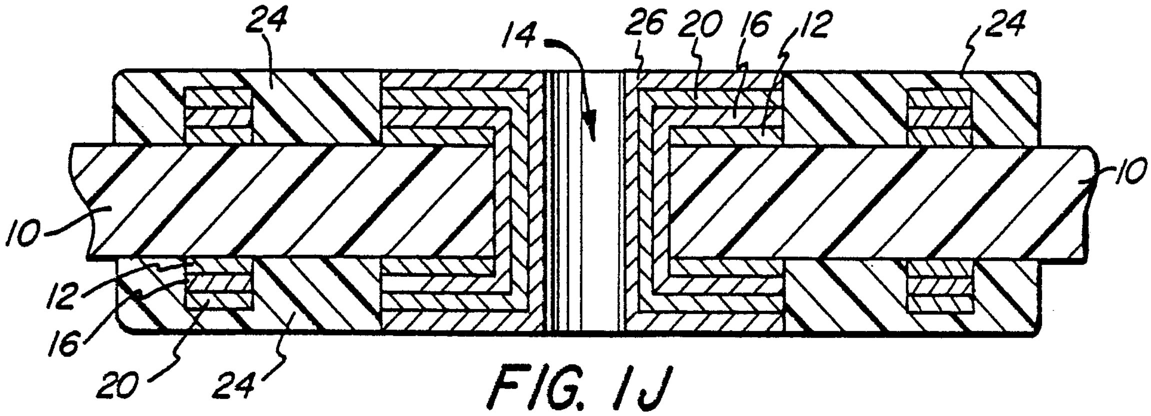
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FIG. 1J

INTERNATIONAL SEARCH REPORT

International Application No PCT/US87/01433

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (4): H01L 21/306
U.S. Cl. 156/632

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	156/632, 656, 659.1, 661.1, 666, 902; 29/852; 427/97; 174/68.5

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	US, A. 3,677,949 (Brindisi Jr.) 18 July 1972 See entire document, particularly column 1, lines 45-55	1-16
Y	US, A, 4,487,654 (Coppin) 11 December 1984 See column 5, lines 2-5	1-16
Y	US, A, 4,144,118 (Stahl) 13 March 1979 See entire document	12, 13
A, P	US, A, 4,608,274 (Wooten) 26 August 1986	
A	US, A, 4,325,780 (Schults Sr.) 20 April 1982	
A	US, A, 4,104,111 (Mack) 01 August 1978	

* Special categories of cited documents: [15]
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
20 July 1987	24 AUG 1987
International Searching Authority [1]	**Signature of Authorized Officer** [20]
ISA/US	Lori - Ann Cody

Form PCT/ISA/210 (second sheet) (May 1986)