

PROCESS FOR METALLIZING NON-CONDUCTING SURFACES AND THE USE OF HYDROXYMETHYLSULFINIC ACID IN THAT PROCESS

The invention is directed to a process for metallizing non-conducting surfaces and the use of hydroxymethylsulfonic acid for this process.

The use of metal-coated non-conducting materials as printed circuit boards is very common. In so doing, layers with electrical pathways or conductor paths always alternate with layers of non-conducting material. Bore holes are arranged at suitable locations for electrically connecting conductor paths of different layers. These bore holes may penetrate the materials completely or only partially (so-called pocket holes). The electrical interconnections between the different conductor paths are produced by metallizing the bore holes.

A wide variety of methods are known for this purpose. The methods most commonly used at present still make use of an electroless (chemical) metallizing bath for metallizing the non-conducting supporting board or base material. This is very often a copper bath, but chemically-depositing nickel baths are also used. Such electroless metallizing baths have a number of disadvantages. They work with chemicals whose handling is problematic and which are expensive to dispose of, e.g. formalin and complexing agents (EDTA, etc.). The cost of supervising these baths is substantial. The baths can be stored only for a very limited time and consume a great amount of chemicals.

For this reason, processes have been developed increasingly over recent years which do not make use of the electroless metal deposition step:

1. Coating the bore hole walls with a layer of carbon particles and subsequent electroplating. The process is non-selective and coats conducting and non-conducting materials equally well. Accordingly, a separating layer of carbon is formed between the conductor paths and bore hole walls when contacting. Cracks can occur at these locations in inner layers due to thermal or mechanical loading of the printed circuit board (EP-A 244535).
2. Production of a conductive polymer layer from the bore hole wall. This process requires a great expenditure on apparatus and is subject to restrictions with respect to the base materials which can be employed.



3. Coating of non-conducting materials with a layer of nonmetallic chalcogenide (generally sulfide) and subsequent electrodeposition (US-4952286, US-4919768, US-4810333, EP 298298). This process is likewise nonselective and also coats the copper surfaces with a sulfide layer which must be removed subsequently in an additional process step.
4. Treatment of catalytically activated surfaces with nitrogen-containing organic compounds prior to electrodeposition (DE-OS 3741 459).

Further, a number of processes are known which employ a colloidal palladium/tin catalyst to produce a slight base conductivity on a non-conducting surface which is just sufficient for applying a metal directly to this surface (EP-A-248683, DE-3323476, DE-3304004, US-3099608, EP-A-398019, DE-3339946). A disadvantage in these systems consists in the high acid content and chloride content in the Pd/Sn catalyst. This invites corrosion on the oxide boundary layer between the copper and nonconductor and the treated printed circuit boards are susceptible to red ring defects. Also, in order to contact the inner layers without defects, the tin hydroxide must be removed as completely as possible from the copper inner layers. However, a minimum of tin must remain on the resin of the bore holes, without which a complete copper coating cannot be achieved in subsequent electrodeposition. As a result of these contradictory requirements, this process is not suitable for producing high-quality printed circuit boards.

The object of the present invention is to develop a process for contacting printed circuit boards which does not use a chemical electroless metallization bath and which selectively coats only the non-conducting surface with a catalytic layer and, at the same time, works without dependence on the substrate.

This object is met by the process according to the invention by the following process steps:

1. Conditioning of the bore hole wall by means of a chelating agent and/or a cationic, surface-active substance.



2. Treatment of the printed circuit board with a colloidal acidic solution of a precious metal which has been stabilized with an organic polymer.
3. Activation of the catalytic layer by means of a solution of a sulfur compound containing sulfur in an oxidation state between +1 and +5, e.g. with sulfinic acid, sulfites, bisulfites, thiosulfates, hydroxymethylsulfites, dithionites, dithionates or tetrathionates.
4. Electrodeposition until a desired layer thickness is reached. As set forth in claim 1, etch-cleaning can be carried out prior to and after step 1 and a treatment with a pre-immersion solution can be effected prior to step 2.

The materials are subjected to cleaning and pre-treatment processes prior to the metallization process. All known so-called desmear and cleaning processes and combinations thereof can be used for cleaning the bore hole surface. Known desmear processes work with sulfuric acid, chromic acid or preferably permanganate. It is also possible to treat the surface in a plasma. Cleaning processes work with alkaline and/or acidic solutions containing at least one surface-active substance from the class of anionic surfactants, nonionic surfactants, cationic surfactants, ampholytes or polyelectrolytes, nonionic or cationic polymers.

Suitable conditioners are the same substances which are suitable for processes with electroless metallization baths, primarily cationic wetting agents such as trimethylalkyl ammonium halides, cationic polyelectrolytes such as quaternary polyvinylimidazole or nitrogen-containing chelating agents such as triethanolamine.

Colloids of palladium, platinum, rhodium, ruthenium, silver and gold can be used as precious metal colloids, palladium being particularly preferred. The concentration of metal in the baths used according to the invention can be between 50 mg/l and several grams per liter, wherein the concentration forms the upper limit for the economic efficiency of the process. Very good results are generally achieved with concentrations between 100 and 500 mg/l. The colloids are stabilized with an ionic or nonionic, soluble organic polymer. Suitable polymers are natural substances such as proteins, peptides, polysaccharides, gelatins, agar, gum arabic, tannin or synthetic polymers such as polyvinylpyridine, polyvinyl alcohol, polyvinyl acetate,



polyethylene glycol, polyimines, polyacrylic acid, polyacrylamide, polyacrylates, polyvinylpyrrolidone, polyvinyl methyl ketone and copolymers and mixtures of these components. Polyvinylpyrrolidone is particularly suitable. The molecular weight of the polymers can be between 1,000 and 10,000,000. The ratio of metal to polymer can be between 3:1 and 1:100, preferably between 1:1 and 1:10.

The production of such colloids is described in EP-A-187962 and EP-A-163831 and DE-PS 37 41 459.

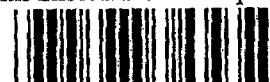
For reasons of cost and ease of use, it is advantageous to use water as solvent for the colloid. However, it is also technically possible to use an organic solvent or mixtures of a combination of these solvents or a mixture of solvent and water.

Subsequent electrodeposition of the bore holes is facilitated when the metal colloid contains chloride ions, bromide ions, or iodide ions (0.1 to 50 g/l). A uniform metallization can be achieved after appreciably shorter electroplating times.

Electrodeposition is likewise improved in the treatment of the printed circuit boards with the metal colloid at increased temperatures. A temperature in the range of 50 to 80° C has proven advantageous. However, the process according to the invention can be carried out in principle at all temperatures between the solidification point and boiling point of the solvent which is used.

The pH of the metal colloid has a decisive influence on the ability to metallize the nonmetallic surface treated with it. The best results are achieved with pH values in the acidic range between 1 and 3, the optimum pH is between 1.5 and 2.

When colloids with acidic pH values are used, the metal may be slowly oxidized and dissolved again due to atmospheric oxygen or carried over oxidants, particularly with lower grades of precious metals such as silver, palladium and ruthenium. The carry-over of oxidants is prevented by treating the printed circuit board with a diluted solution of reducing agent prior to treating with the metal colloid. In addition, it is advantageous to add generally small amounts of reducing agent to the metal colloid. An embodiment form in which the reduction potential in the metal colloid solution is permanently monitored by means of an electrode and maintained at a constant value by automatic repeated dosing of reducing agent is particularly preferred. This procedure has proven advantageous particularly also with reducing agents



(e.g. borane compounds, hypophosphite) which are catalytically decomposed by the precious metal colloid. In this case, the hydrogen occurring as a result of decomposition serves as a buffer against oxidants.

The catalytic precious metal layer applied in this way can be activated in an additional step. This considerably simplifies electrodeposition. This step is characterized in that compounds are used which only act on the catalytic precious metal layer and do not change the copper surfaces. This is achieved by diluted solutions of compounds containing sulfur in an oxidation state, where (Ox) $0 < \text{Ox} < 6$. This includes, for example, sulfonic acids, sulfinic acids, sulfoxides, sulfones, sulfites, dithionites, dithionates and tetrathionates. Sulfinic acids, in particular hydroxymethanesulfinic acids are particularly suitable for this purpose.

The printed circuit boards treated in this way can now be electroplated in an optional metallizing bath without additional processing. Copper is particularly preferred because of its superior conductivity, but it is also possible to employ a different metal if desired. Mat-copper baths have proven particularly advantageous. The surfaces to be metallized are accordingly completely coated with a continuous metallic layer within a particularly short period of time.

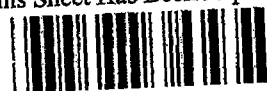
Example 1: Production of the catalyst

Solution a: PdCl_2 (1.7 g) is dissolved in 40 ml (10-200 ml) 20-percent hydrochloric acid with gentle heating, when appropriate. This solution is then diluted with up to 1 liter of water. Water is then added to this solution until it amounts to 3 liters.

Solution b: 10 g (5-100 g/l) of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ are dissolved in 1 liter of water.

Solution b is then added to solution a accompanied by vigorous stirring. After a short time, the solution begins to darken and total development takes place. The reaction is terminated when the gas generation has concluded. After adjusting the pH to 1.8 (0.8-3.5) with hydrochloric acid or caustic solution, the solution is ready to use.

No settling of the palladium particles is observed even after long storage times and at high temperatures. If the solution comes in extensive contact with air over a longer period of



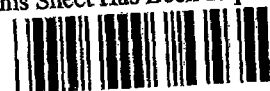
time, the palladium solution may be reversed. In this case, the catalyst can be regenerated by adding 2 g/l sodium hypophosphite.

Example 2

Polyvinylpyrrolidone K60 is used instead of polyvinylpyrrolidone K15. A catalyst with good catalytic properties and excellent stability is obtained.

Example 3: Process sequence with smear removal

Process step	Contents	T	Processing time
1. swelling swelling agent Securiganth P* pH adjusting solution CC*	500 ml/l .23 ml/l	65° C	5 min
1a. rinse			
2. potassium permanganate etching potassium permanganate potassium manganate sodium hydroxide	60 g/l 20 g/l 40 g/l	65° C	10 min
2a. rinse			
3. cleaning/conditioning reduction cleaner Securiganth P* hydrogen peroxide (30%)	100 ml/l 15 ml/l	RT	5 min
3a. rinse			
4. etch-cleaning etching cleaner Securiganth C* sulfuric acid (d=1.84) wetting agent G13*	40 g/l 10 ml/l 2 ml/l	RT	2 min
4a. rinse			
5. pre-immersion sodium hypophosphite	1 g/l	RT	1 min
6. catalysis		75° C	10 min
6a. rinse			
7. re-immersion hydroxymethane sulfinic acid	2 g/l	RT	2 min
7a. rinse			



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8.	pickling sulfuric acid (d=1.84)	50 ml/l	RT	1 min
9.	copper plating Cupracid BL-CT		RT	

According to this example, contacted double-sided and multiple-layer printed circuit boards of epoxy resin with paper or glass fiber reinforcement, polyimide or Teflon have excellent quality and do not show defects in the copper-plating of different materials or in the contacting of inner layers.

Example 4: Process corresponding to example 3 without steps 7 and 7a.

Printed circuit boards treated in this way also have an outstanding quality. However, when the electrodeposition of metal layers is carried out precisely a complete coating of the bore hole walls with copper is observed to last longer than in example 3.

Example 5: Process sequence without smear removal

Process step	Contents	T	Processing time
1.	etch-cleaning etching cleaner Securiganth *	RT	2 min
	H ₂ SO ₄ (d=1.84)		
	sulfuric acid (d=1.84)		
	wetting agent G13*		
1a.	rinse	65° C	10 min
2.	conditioning triethanolamine		
	10 g/l		
2a.	rinse	RT	1 min
3.	pre-immersion sodium hypophosphite		
	3 g/l		
4.	catalysis (see Example 1)	65° C	10 min
4a.	rinse		

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5.	re-immersion		RT	2 min
	hydroxymethane sulfinic acid	5 g/l		
5a.	rinse			
6.	pickling		RT	1 min
	sulfuric acid	50 ml/l		
	(d=1.84)			
7.	copper plating		RT	10 min
	Cupracid BL-CT*1			

Flexible, rigid-flexible or rigid double-sided and multiple-layer printed circuit boards of epoxy resin with paper or glass fiber reinforcement, polyimide, thermoplastics or ceramics treated according to this example are contacted without defects. No tarnishing of the copper plating can be observed during or after treatment with the post-immersion solution. The copper surfaces are dyed bright pink.

Example 6:

Method corresponding to example 5 with a conditioner composed of sodium carbonate (5 g/l) and Basotronic PVI (5 g/l) (a product of BASF AG, Ludwigshafen).

Printed circuit boards treated according to this method show the same good results as those treated according to examples 3 to 5.

Example 7:

Process corresponding to example 5 or 6 with a re-immersion solution of 10 g/l sodium thiosulfate instead of hydroxymethane sulfinic acid. Printed circuit boards treated in this way can be metallized with excellent results.

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Example 8:

Process sequence corresponding to example 5.

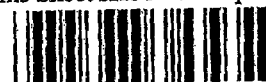
A 5 cm x 5 cm plate of FR4 material laminated on one side is used as a test board. After electroplating with copper for 10 min at 2 amperes/dm², the side of the plate not coated with copper is covered with a copper coating of approximately 1 cm proceeding from the edges.

Example 9:

This example serves as a comparison between the process according to the invention and the known process based on a palladium/tin catalyst. A process corresponding to example 8 is used, in which a commercial hydrochloric acid palladium/tin catalyst (Noviganth Activator AK I *, 250 mg/l palladium, 10 min., 25° C) is substituted for the catalyst in step 4 and the re-immersion solution in step 5 is replaced by a 2-percent tetrafluoroboric acid solution (5 min., RT). The test board is also covered by a copper coating of only a few millimeters at the edges after 10 min. at 2A/dm².

Remarks:

Aqueous solutions of the indicated ingredients are used in all process examples. The indicated concentrations of ingredients can also often be reduced or increased by a factor of two to five without noticeably affecting the contacting results. This is also true of the treatment times. Temperatures can often be varied by 10° to 20° C without a substantial influence on the results of the process.

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CLAIMS

1. Process for metallizing non-conducting surfaces, characterized by the following steps
 - a) etch-cleaning, where appropriate,
 - b) conditioning with a chelating agent and/or a cationic surface-active substance,
 - c) etch-cleaning, where appropriate,
 - d) treatment with a pre-immersion solution, where appropriate,
 - e) treatment with a colloidal acidic solution of a precious metal, which solution is stabilized with an organic polymer,
 - f) treatment with a solution containing one or more sulfur compounds such as sulfinic acid, sulfites, bisulfites, thiosulfates, dithionites, dithionates and/or tetrathionates,
 - g) electrodeposition of metal layer.
2. Process according to claim 1, wherein the colloidal acidic solution of a precious metal stabilized with an organic polymer contains acid, precious metal(s) and/or salts of precious metal, an organic protective colloid and a reducing agent.
3. Process according to claim 1 or 2, wherein palladium, platinum, rhodium, ruthenium, silver and gold are used as precious metals.
4. Process according to claim 1, wherein polyvinylpyridine, polyvinyl alcohol, polyvinylpyrrolidone, polyvinyl acetate, polyacrylates or copolymers or mixtures are used as organic polymers.
6. Process according to claim 1, wherein quaternized polyvinylimidazole, triethanolamine or monoethanolamine is used as conditioner.
7. Use of hydroxymethylsulfinic acid for metallizing non-conducting surfaces.

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