

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.

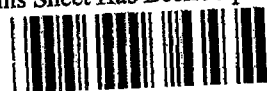
Example 1: Production of the catalyst

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



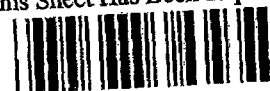
time, the palladium solution may be reversed. In this case, the catalyst can be regenerated by adding 2 g/l sodium hypophosphite.

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.

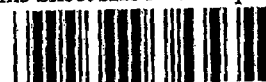
A 5 cm x 5 cm plate of FR4 material laminated on one side is used as a test board. After electroplating with copper for 10 min at 2 amperes/dm², the side of the plate not coated with copper is covered with a copper coating of approximately 1 cm proceeding from the edges.

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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ABSTRACT

The invention is directed to a 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, where appropriate,
- g) electrodeposition of metal layer.

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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.

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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).

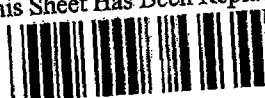
Further, a number of processes are known which employ a colloidal palladium/tin catalyst to produce a slight base conductivity on a non-conducting surface which is just sufficient for applying a metal directly to this surface (EP-A-248683, DE-3323476, DE-3304004, US-3099608, EP-A-398019, DE-3339946). 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:

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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,



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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



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(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 $(Ox) 0 < Ox < 6$. 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 $NaH_2PO_2 \cdot H_2O$ 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

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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		65°C	5 min
swelling agent Securiganth P*	500 ml/l		
pH adjusting solution CC*	.23 ml/l		
1a. rinse			
2. potassium permanganate etching		65°C	10 min
potassium permanganate	60 g/l		
potassium manganate	20 g/l		
sodium hydroxide	40 g/l		
2a. rinse			
3. cleaning/conditioning		RT	5 min
reduction cleaner	100 ml/l		
Securiganth P*			
hydrogen peroxide (30%)	15 ml/l		
3a. rinse			
4. etch-cleaning		RT	2 min
etching cleaner	40 g/l		
Securiganth C*			
sulfuric acid (d=1.84)	10 ml/l		
wetting agent G13*	2 ml/l		
4a. rinse			
5. pre-immersion		RT	1 min
sodium hypophosphite	1 g/l		
6. catalysis		75°C	10 min
6a. rinse			
7. re-immersion		RT	2 min
hydroxymethane sulfinic acid	2 g/l		
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		
2.	conditioning triethanolamine	65° C	10 min
2a.	rinse		
3.	pre-immersion sodium hypophosphite	RT	1 min
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 (Novigant 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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REPLACEMENT SHEET
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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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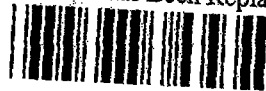
PROCESS FOR METALLIZING NON-CONDUCTING SURFACES AND THE
USE OF HYDROXYMETHYLSULFINIC ACID IN THAT PROCESS

ABSTRACT

The invention is directed to a 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, where appropriate,
- g) electrodeposition of metal layer.

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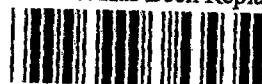
03 DEC 1997

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CLAIMS

1. Method of metallising non-conductive surfaces, characterised by the following steps:
 - a) possible etch-cleaning,
 - b) conditioning by a chelate former and/or cationic, surface-active substance,
 - c) possible etch-cleaning,
 - d) possible treatment with a preliminary immersion solution,
 - e) treatment with a colloidal acidic solution of a precious metal, which solution is stabilised by an organic polymer,
 - f) treatment with a solution which contains, as one or more sulphur compounds, sulphinic acid, sulphites, bisulphites, thiosulphates, dithionites, dithionates and/or tetrathionates, and
 - g) galvanic metallisation.
2. Method according to claim 1, wherein the colloidal acidic solution of method step e) is produced by mixing acid, precious metal and/or precious metal salt, organic protective colloid and a reducing agent in a solvent.
3. Method according to claim 1 or 2, wherein palladium, platinum, rhodium, ruthenium, silver and gold are used as the precious metals.
4. Method according to claim 1, wherein polyvinyl pyridine, polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl acetate, polyacrylates or copolymers or mixtures are used as the organic polymer.
5. Method according to claim 1, wherein quaternary polyvinyl imidazole, triethanol amine or monoethanol amine is used as the conditioning agent.

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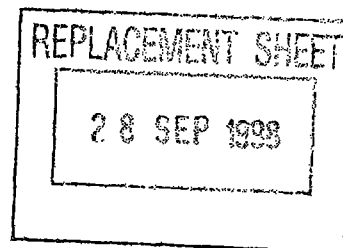
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6. Use of hydroxymethane sulphinic acid in a method for metallising non-conductive surfaces.



* C L M S *



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

The invention relates to a method of metallising non-conductive surfaces and the use of hydroxymethane sulphinic acid in the method.

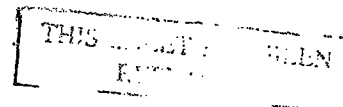
The use of metal-coated, non-conductive materials as a printed circuit board is widely known. In such case, layers with conductor paths and layers of non-conductive always alternate with one another. Bores are provided at suitable locations for the electrical connection of conductor paths of different layers. Such bores may penetrate the material fully or even only partially (so-called blind-bores). The electrical connections between the different conductor paths are established by metallising the bores.

A large number of various methods have been disclosed for this purpose. The methods which utilise a metallisation bath, which (chemically) deposits without external current, are still at present the most frequently used methods. Very often this bath is a copper bath, but chemically depositing nickel baths are also used. Such metallisation baths, without external current, have several serious disadvantages: They operate with chemicals which are difficult to handle, and they are expensive to obtain, such as, for example, formaline and complex formers (EDTA et al.). The monitoring outlay for these baths is considerable, since the baths have only a very limited service-life and a very high consumption of chemicals.

In consequence, methods have been intensively developed in recent years which operate without the electroless metallic deposition step:

1. Covering the bore walls with a layer of carbon particles and subsequent galvanic metallisation. The method is unselective and equally covers conductive and non-conductive materials. A separation layer of carbon is

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REPLACEMENT SHEET
28 SEP 1995

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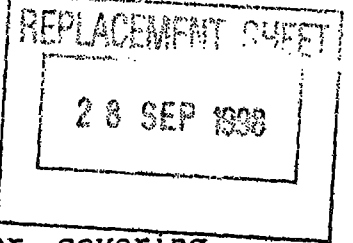
thereby produced when there is contact between the conductor paths and the bore sleeve. Internal cracks in the layers may then occur at these locations in the event of the printed circuit board being thermally or mechanically loaded (EP-A 244535).

2. Producing a conductive polymer layer from the bore wall. This method is associated with complex prerequisites in respect of apparatus and is subjected to restrictions with regard to the processable base materials.

3. Covering the non-conductive material with a layer of non-metallic chalcogenide (generally sulphide) and subsequent galvanic metallisation (US-4952286, US-4919768, US-4810333, EP 298298). The method is also unselective and also covers the copper surfaces with a layer of sulphide, which must be removed again in an additional process step.

4. Treating catalytically activated surfaces prior to the galvanic metal deposition with nitrogen-containing organic compounds (DE-OS 3741 459).

Furthermore, a number of methods have been disclosed, which utilise a colloidal palladium/tin catalyst, in order to produce a low basic conductivity on a non-conductive surface, just sufficient to deposit a metal galvanically directly thereon (EP-A-248683, DE-3323476, DE-3304004, US-3099608, EP-A-398019, DE-3339946). These systems are disadvantageous because of the high content of acid and chlorides in the Pd/Sn catalyst. A contact with the oxide boundary layer between copper and non-conductor is hereby rendered possible, and the treated printed circuit boards are susceptible to the Rotring fault. In order to obtain a faultless contact between the internal layers, the zinc hydroxide must also be removed as fully as possible from the internal copper layers. However, a minimum quantity of zinc must remain behind on the resin of



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the bores since, otherwise, a complete copper covering cannot be achieved during subsequent galvanising. These contradictory demands lead to these methods not being suitable for the production of high-quality printed circuit boards. The basic object of the invention is to develop a method of plating-through printed circuit boards without a metallisation bath, which is chemically without an external current, and such bath selectively only covers the non-conductive surfaces with a catalyst layer and simultaneously operates independently of a substrate.

This object is achieved by the method according to the invention, having the following method steps:

1. Conditioning the bore surface by a chelate complex former and/or a cationic, surface-active substance.
2. Treating the printed circuit board with a colloidal acidic solution of a precious metal, which solution is stabilised by an organic polymer.
3. Activating the catalytic layer by a solution which contains, as one or more sulphur compounds, sulphinic acid, sulphites, bisulphites, thiosulphates, hydroxymethyl* sulphites, dithionites, dithionates or tetrathionates.
4. Galvanic metallisation to the desired layer thickness. According to claim 1, an etch-cleaning may be effected before and after step 1, and a treatment with a preliminary immersion solution may be effected before step 2.

Prior to the metallisation process, the materials are subjected to a cleaning and pretreatment method. All

*Translator's note

Perhaps "hydroxymethyl" should be "hydroxymethane".

known so-called desmearing and cleaning methods, as well as combinations thereof, may be used to clean the bore surface. Known desmearing methods operate with sulphuric acid, chromic acid or preferably permanganate. A treatment of the surface in a plasma is also possible. Cleaning methods operate with alkaline and/or acidic solutions, which contain at least one surface-active substance from the class of anionic surfactants, non-ionic surfactants, cationic surfactants, ampholytes or polyelectrolytes, non-ionic or cationic polymers.

The same substances, which are also suitable for methods with electroless metallisation baths are suitable as the conditioning agents. Primarily suitable here are cationic cross-linking agents such as trimethyl alkyl ammonium halides, cationic polyelectrolytes such as quaternary polyvinyl imidazole, or nitrogen-containing chelate complex formers such as triethanol amine.

Colloids of the metals palladium, platinum, rhodium, ruthenium, silver and gold may be used as the precious metal colloid, palladium being quite specifically preferred. The concentration of the metal in the baths used according to the invention may be between 50 mg/l and several grams per litre, the economic efficiency of the method limiting the concentration upwardly. Very good results are generally obtained with concentrations between 100 and 500 mg/l. The colloids are stabilised with an ionic or non-ionic, soluble organic polymer. Natural substances are suitable therefor, such as, for example, proteins, peptides, polysaccharides, gelatins, agar-agar, rubber arabicum, tannin or even synthetic polymers such as polyvinyl pyridine, polyvinyl alcohol, polyvinyl acetate, polyethylene glycol, polyimines, polyacrylic acid, polyacryl amide, polyacrylates, polyvinyl pyrrolidone, polyvinyl methyl ketone, as well as copolymers and mixtures of these components. Polyvinyl pyrrolidone is particularly

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suitable. The molecular weight of the polymers may be between 1,000 and 10,000,000. The ratio of metal:polymer may be between 3:1 and 1:100, and the range between 1:1 and 1:10 is preferred.

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

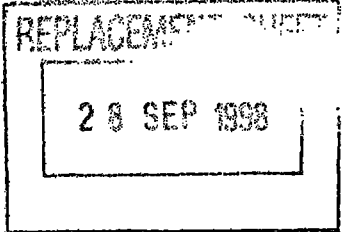
Both because of the costs and because of the simpler handling, it is advantageous when the solvent for the colloid is water. However, the use of an organic solvent or mixtures thereof with themselves or with water is also technically possible.

A content in the metal colloid of chloride, bromide or iodide ions of between 0.1 and 50 g/l facilitates the subsequent galvanic metallisation of the bores. A uniform covering of metal can already be achieved after distinctly shorter galvanising times.

High temperatures when treating the printed circuit boards with the metal colloid also improve the galvanisability. A temperature in the range of between 50 and 80° C has proved to be an advantageous embodiment. Basically, however, the method according to the invention can be effected at all temperatures between the hardening point and the boiling point of the solvent used.

The pH value of the metal colloid is crucial for the galvanisability of the non-metal surfaces treated therewith. Best results are obtained with pH values in the acidic range of between 1 and 3, with an optimum at 1.5 to 2.

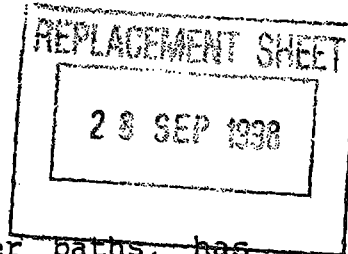
If the colloids are used with acidic pH values, a slow oxidation and redissolving of the metal by air oxygen or retarded oxidising agent result, especially in the case



of less noble precious metals such as silver, palladium and ruthenium. By treating the printed circuit boards with a dilute solution of a reducing agent prior to the treatment with the metal colloid, the introduction of oxidising agents is prevented. It is additionally advantageous to add small quantities of reducing agent regularly to the metal colloid. One embodiment is particularly preferred, wherein the reduction potential in the metal colloid solution is permanently monitored by means of an electrode and kept to a constant value by automatically topping-up the reducing agent. This procedure has proved to be advantageous, especially also with the reducing agents (such as, for example, boron hydrogen compounds, hydrophosphite), which are catalytically decomposed by the precious metal colloid. In this case, the hydrogen produced during the decomposition takes over the buffering against oxidising agents.

The catalytic precious metal layer, thus applied, can be activated in a further step. The galvanic metallisation is substantially facilitated hereby. Characteristic for this step is the fact that compounds are used which only act on the catalytic precious metal layer and do not change the copper surfaces. This is achieved by dilute solutions of compounds which contain sulphur in an oxidation stage, for which $0 < Ox < 6$ applies. Sulphonic acids, sulphinic acids, sulfoxides, sulphones, sulphites, dithionites, dithionates and tetrathionates, which are used according to the invention, fall into this class. Sulphinic acids, more especially hydroxymethane sulphinic acid, are particularly suitable.

The printed circuit boards, thus treated, can now be galvanised in any desirable galvanic metallisation bath without further treatment. Because of the particularly good conductivity of this metal, a copper coating is particularly preferred, but other metals can also be



applied if desired. The use of matt copper baths, has proved to be particularly advantageous. The surfaces to be metallised are hereby already covered completely with a full metal layer after a particularly short time.

Example 1: Production of the catalyst

Solution a: 1.7 g PdCl_2 are dissolved in 40 ml (10-200 ml) 20% hydrochloric acid, possibly with slight heating. The solution is subsequently diluted with water to 1 litre. Polyvinyl pyrrolidone K15 is added to this solution and topped-up with water to 3 litres after the dissolving process.

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

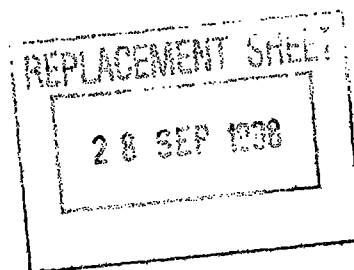
Solution b is added to solution a with intensive stirring. After a short time, the solution begins to darken, and a development of gas occurs. The reaction is terminated when the development of gas is terminated. After adjusting the pH with hydrochloric acid or soda lye to 1.8 (0.8 - 3.5), the solution is ready for use.

Even after long storage periods and at high temperatures, the palladium particles cannot be seen to settle.

If the solution has come into contact with air intensively for a relatively long time, a resolution of the palladium may occur. In this case, the catalyst can be regenerated by the addition of 2 g/l sodium hypophosphite.

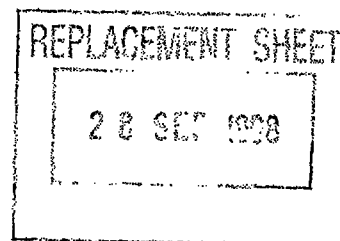
Example 2

Polyvinyl pyrrolidone K60 is used instead of polyvinyl pyrrolidone K15. A catalyst is also obtained with good catalytic properties and excellent stability.



Example 3: Method with smear removal

Method Step	Content	T	Treatment Time
1. Soaking		65°C	5 min
Soaker Securignath P*	500 ml/l		
pH Correction Solution CC*	23 ml/l		
1a. Rinsing			
2. Potassium permanganate etching		65°C	10 min
Potassium permanganate	60 g/l		
Potassium manganate	20 g/l		
Sodium hydroxide*	40 g/l		
2a. Rinsing			
3. Cleaning/Conditioning		RT	5 min
Reduction Cleaner	100 ml/l		
Securignath P*			
Hydrogen peroxide (30%)	15 ml/l		
3a. Rinsing			
4. Etch-cleaning		RT	2 min
Etch Cleaner	40 g/l		
Securignath C*			
Sulphuric Acid (d=1.84) *	10 ml/l		
wetting agent G13	2 ml/l		
4a. Rinsing			
5. Preliminary immersion		RT	1 min
Sodium hypophosphite	1 g/l		
6. Catalysing		75°C	10 min
6a. Rinsing			
7. Subsequent immersion		RT	2 min
Hydroxymethane sulphinic acid	2 g/l		
7a. Rinsing			
8. Pickling		RT	1 min
Sulphuric acid	50 ml/l		
(d=1.84)			
9. Galvanic Copper ..		RT	
Cupracid BL-CT			



According to this Example, plated-through, double-sided and multiple-layered printed circuit boards formed from epoxy resin with paper or glass fibre reinforcement, polyimide or Teflon are of excellent quality and exhibit neither faults in the covering of the various materials with copper nor contact with internal layers.

Example 4: Method according to Example 3 without steps 7 and 7a.

Printed circuit boards, thus processed, are also of high quality. If the galvanic metal deposition is pursued accurately, however, it can be ascertained that a full covering of the bore sleeves with copper lasts longer than in Example 3.

Example 5: Method without smear removal

Method Step	Content	T	Treatment Time
1. Etch-cleaning		RT	2 min
Etch Cleaner	200 g/l		
Securignath *			
H ₂ SO ₄ (d=1.84)	10 ml/l		
<u>Wetting agent G13*</u>	2 ml/l		
1a. Rinsing			
2. Conditioning		60°C	5 min
Triethanol amine	10 g/l		
2a. Rinsing			
3. Preliminary immersion		RT	1 min
Sodium hypophosphite	3 g/l		
4. Catalysing		65°C	10 min
(see Example 1)			
4a. Rinsing			
5. Subsequent immersion		RT	2 min

Hydroxymethane sulphinic acid 5 g/l

5a. Rinsing

6. Pickling RT 1 min

Sulphuric acid (d=1.84) 50 ml/l

7. Galvanic Copper RT 10 min

Cupracid BL-CT*1

Flexible, rigid-flexible or rigid, double-sided and multiple-layered printed circuit boards, treated according to this Example and formed from epoxy resin with paper and/or glass fibre reinforcement, polyimide, thermoplastics materials or ceramics are satisfactorily plated-through. During and after the treatment with the subsequent immersion solution, no accumulation of the copper coating is to be observed; rather, the copper surfaces are coloured pale pink.

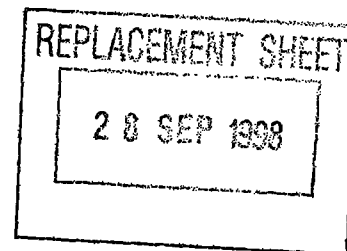
Example 6:

Method corresponding to Example 5 with a conditioner formed from 5 g/l sodium carbonate and 5 g/l Basotronic PVI (product produced by BASF AG, Ludwigshafen).

Printed circuit boards, treated according to this method, exhibit the same good results as those treated according to Examples 3 to 5.

Example 7:

Method corresponding to Example 5 or 6 with a subsequent immersion solution formed from 10 g/l sodium thiosulphate instead of hydroxymethane sulphinic acid. Printed circuit boards, thus treated, can be metallised galvanically in a satisfactory manner.



Example 8:

Method corresponding to Example 5.

As a test board, a small board is used, which has dimensions of 5 cm x 5 cm and is formed from unilaterally coated FR4 material. After a galvanic copper-plating of 10 mins. with 2 ampere/dm², the small board is covered with copper on the non-copper-coated side approx. 1 cm from the edges.

Example 9:

This Example serves to compare the method according to the invention with known methods which are based on a palladium/tin catalyst. A method corresponding to Example 8 is used therefor. The catalyst is only exchanged in step 4 for a commercially available hydrochloric acid palladium/tin catalyst (Novigant Activator AK I *, 250 mg/l palladium, 10 mins., 25° C), and the subsequent immersion solution is replaced by a 2 % tetrafluoroboric acid solution in step 5 (5 mins., RT). Also after 10 mins. at 2A / dm², the small test board is covered with copper over only a few millimetres at the edges.

Remarks:

All of the method examples involve aqueous solutions of the listed contents. The given concentrations of the contents can often be exceeded or not reached by a factor of between two and five without any visible effects on the result of the through-plating. The same applies to the given treatment times. Temperatures may often be varied by 10 to 20° C without any great influence on the result of the methods.

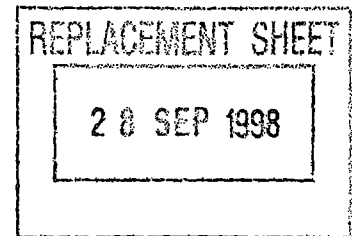
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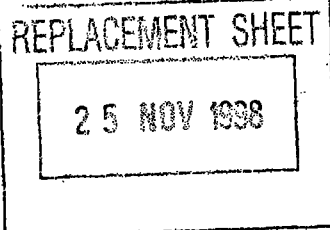
CLAIMS

1. Method of metallising non-conductive surfaces, characterised by the following steps:
 - a) possible etch-cleaning,
 - b) conditioning by a chelate former and/or cationic, surface-active substance and/or cationic polyelectrolyte
 - c) possible etch-cleaning,
 - d) possible treatment with a preliminary immersion solution,
 - e) treatment with a colloidal acidic solution of a precious metal, which solution is stabilised by an organic polymer,
 - f) treatment with a solution which contains, as one or more sulphur compounds, sulphinic acid, sulphites, bisulphites, thiosulphates, dithionites, dithionates and/or tetrathionates, and
 - g) galvanic metallisation.
2. Method according to claim 1, wherein the colloidal acidic solution of method step e) is produced by mixing acid, precious metal and/or precious metal salt, organic protective colloid and a reducing agent in a solvent.
3. Method according to claim 1 or 2, wherein palladium, platinum, rhodium, ruthenium, silver and gold are used as the precious metals.
4. Method according to claim 1, wherein polyvinyl pyridine, polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl acetate, polyacrylates or copolymers or mixtures are used as the organic polymer.
5. Method according to claim 1, wherein quaternary polyvinyl imidazole, triethanol amine or monoethanol amine is used as the conditioning agent.



7. Use of hydroxymethane sulphinic acid in a method for metallising non-conductive surfaces.





REPLACEMENT SHEET

- 1 -

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

The invention relates to a method of metallising non-conductive surfaces and the use of hydroxymethane sulphinic acid in the method.

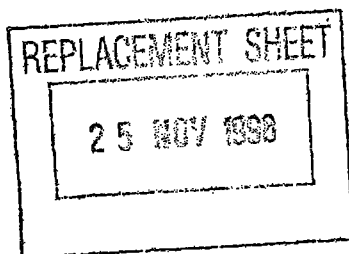
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A large number of various methods have been disclosed for this purpose. The methods which utilise a metallisation bath, which (chemically) deposits without external current, are still at present the most frequently used methods. Very often this bath is a copper bath, but chemically depositing nickel baths are also used. Such metallisation baths, without external current, have several serious disadvantages: They operate with chemicals which are difficult to handle, and they are expensive to obtain, such as, for example, formaline and complex formers (EDTA et al.). The monitoring outlay for these baths is considerable, since the baths have only a very limited service-life and a very high consumption of chemicals.

In consequence, methods have been intensively developed in recent years which operate without the electroless metallic deposition step:

1. Covering the bore walls with a layer of carbon particles and subsequent galvanic metallisation. The method is unselective and equally covers conductive and non-conductive materials. A separation layer of carbon is

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REPLACEMENT SHEET

- 14 -

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

ABSTRACT

The invention is directed to a 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, where appropriate,
- g) electrodeposition of metal layer.