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3,259,559

METHOD FOR ELECTROLESS COPPER PLATING

Filed Aug. 22, 1962

FIG. 1

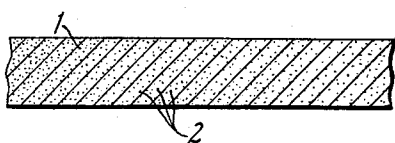


FIG. 2

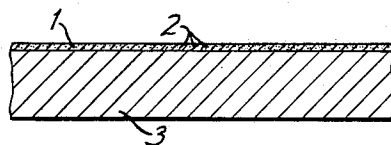


FIG. 3

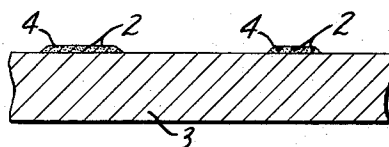


FIG. 4

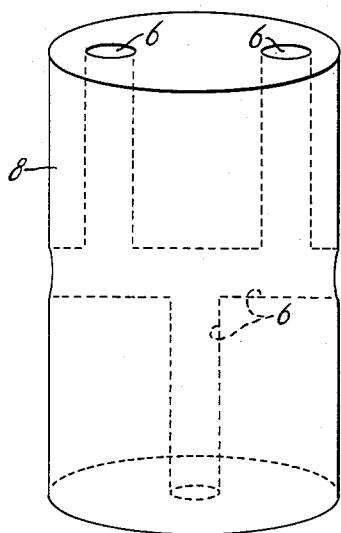


FIG. 4A

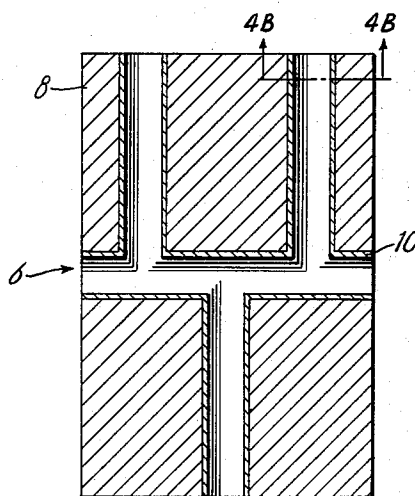
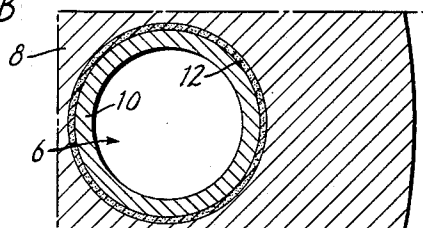


FIG. 4B



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3,259,559

METHOD FOR ELECTROLESS COPPER PLATING
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Filed Aug. 22, 1962, Ser. No. 218,656

The portion of the term of the patent subsequent to June 25, 1980, has been disclaimed
45 Claims. (Cl. 204—38)

The present invention is a continuation-in-part of co-pending applications Ser. No. 785,703, filed January 8, 1959, and now abandoned; Ser. No. 33,361, filed May 31, 1960, now Patent No. 3,146,125; and Ser. No. 26,401, filed May 3, 1960, and now Patent No. 3,095,309.

This invention relates to novel and improved methods for metallizing insulating supports and to the products which result from such methods.

More particularly, the present invention relates to imposing by chemical means strongly adherent and rugged deposits of metal on insulating supports and to the products which result from such methods.

Although applicable whenever it is desired to strongly adhere a metal coating to an insulating base, as for example, for decorative effect, or to make electrical conductors of a wide variety of shapes and configurations, the procedures for metallization disclosed herein are particularly useful for making printed circuits from cheap, low-grade, readily available electrical insulating base materials or base materials coated with electrical insulation materials.

It is a primary object of the present invention to provide improved chemical methods for imposing a uniform, rugged, firmly adherent, non-porous, bright and ductile deposit of copper on an insulating surface.

Another object of the invention is to provide chemical methods for imposing such a deposit of copper on irregularly shaped, complex, or curved insulating surfaces.

Still another object of this invention is to provide improved chemical methods for imposing a rugged and adherent conductor pattern on cheap, readily available insulating base materials.

A further object of this invention is to provide improved printed circuits which are rugged and durable, and which can withstand rough mechanical handling and heat shock.

Another object of this invention is to provide methods for making improved printed circuits in which the support for the circuits has improved insulating properties.

An additional object of this invention is to transform cheap, insulating base materials into commercially attractive electrical conductive components by chemical means.

Other objects and advantages of the invention will be set forth in part herein and in part will be obvious herefrom or may be learned by practice with the invention, the same being realized and attained by means of the steps, instrumentalities and combinations pointed out in the appended claims.

The invention consists in the novel parts, constructions, arrangements, combinations and improvements herein shown and described.

The accompanying drawings referred to herein and constituting a part hereof, illustrate embodiments of the invention and together with the description serve to explain the principles of the invention.

Although the invention will be described with particular reference to printed circuits, and although fabrication of printed circuits constitutes a primary and preferred application, it should be understood that the invention is

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not limited to printed circuits but is applicable to metallizing insulating surfaces broadly.

Heretofore, it has been suggested to manufacture printed circuits by printing on an insulating backing a design of the circuit by means of various inks containing receptive particles and then electrolessly depositing a conductive material on the receptive particles.

Two main problems have been encountered in such a procedure. The first problem concerns the adhesion between the receptive particles and the base. Techniques previously described include seeding a base material with aqueous acidic solutions of precious metal ions such as palladium chloride. For example, the insulating material may be immersed in a bath comprising an aqueous acidic solution of stannous chloride and palladium chloride to render selected areas of the insulating material sensitive to the reception of an electroless metal deposit. Such sensitization baths, however, have many disadvantages. First and foremost, the adhesion between the precious metal deposit and the subsequently electrolessly deposited metal has been found to be tenuous. As a result, when the resulting circuits are subjected to rugged mechanical handling, or heat shock, such as by dip soldering, there is a tendency for the conductive layer to crack or pop free of the base, thereby disrupting the circuit. Additionally, such treating solutions are ponderous and expensive to employ, and must be carefully regulated if good results are to be achieved.

The second problem encountered in metallizing insulating bases by the technique under discussion resides in the electroless metal bath. Heretofore, a wide variety of electroless metal plating bath processes have been proposed for the deposition of thin layers of metal upon insulating surfaces, ceramics, plastics, and other materials. In general, none of these have been useful to any substantial degree for the electroless deposition of copper on metal surfaces. The prior art baths have produced copper deposits which are brittle, break under vibration and bending, and otherwise exhibit poor ductility, although many of the baths are commercially useful within recognized limits. Additionally, the deposits produced by most prior electroless copper depositing baths do not produce copper deposits which are bright. Rather, the deposits from conventional baths ordinarily exhibit a dull surface of poor color. Frequently, the prior art baths yield a "muddy" layer of copper. Additionally, the baths of the prior art processes are often subject to instability, and impurities rapidly accumulate in the baths, the bath finally reaching a condition such that it spontaneously decomposes, throwing out copper as a useless precipitate.

These and other disadvantages of the prior art are overcome by the present invention.

According to this invention, a process for metallizing insulating surfaces has been discovered which comprises providing an insulating base material with adhesively bound, finely divided, solid particles of an agent catalytic to the reception of electroless deposited metal, and then subjecting the resulting base material to a new and improved electroless copper bath to be disclosed.

When the catalytic compositions and the electroless depositing baths described herein are employed in the manner and in the sequence to be described, there is produced on the base material a dense, uniform, ductile, bright, conductive copper deposit which is firmly and tenaciously adhered to the base material or substrate.

It is the combination of the catalytic composition to the electroless copper depositing baths disclosed herein that leads to the production of new and unexpectedly improved coatings of copper on an insulating base.

When the catalytic composition and the electroless copper depositing baths disclosed are employed in making printed circuits, many advantages over the conventional

commercial procedures are obtained. According to this process, copper is applied only where desired. No etching is required, and no copper is thrown away. The process is readily adaptable to mass production techniques, and miniaturized circuits having firmly adherent conductive patterns are obtained. Additionally, the copper deposit forming the conductive pattern is ductile and bright, and its thickness can be controlled to close limits. The fact that the copper deposit is ductile is highly significant. Because of its ductility, the conductor pattern is strongly resistant to both mechanical and thermal shock and can readily withstand both rough mechanical handling and soldering, including dip soldering. Heretofore, so far as applicants are aware, it has not been possible to deposit a ductile copper layer using electroless techniques. Additionally, the process is economical and requires a minimum amount of control. Further, the copper deposit can be applied on practically any base material, regardless of size, shape or configuration, and can be subsequently readily coated or reinforced with other metals by electroless dip techniques or other procedures to impart special characteristics or properties to the circuits as a whole, or portions thereof.

A limiting factor in the production of printed circuits by the conventional print and etch technique is that the thickness of the foil, ordinarily produced by rolling copper, has a lower limit of about 0.7 to 1.3 mils. Frequently, for special purposes, it is desirable to have a conductor pattern which is less than 0.7 mil, i.e., in the order of about 0.1 mil or even lower. With the techniques described herein, uniform layers of ductile copper having a thickness of less than 1.3 mils, or in the order of about 0.1 mil to 7 mils, or even less, may readily be achieved.

The catalytic compositions forming a part of the present invention comprise an adhesive resin base having dispersed throughout finely divided particles of an agent which is receptive to electrolessly deposited copper.

The receptive agents dispersed throughout the resin base are cheap, readily available, particulate, finely divided metal or metal oxides, such as titanium, aluminum, copper, iron, cobalt, zinc, titanous oxide, copper oxide, and mixtures of the foregoing.

Particularly good results are achieved when the receptive agent is cuprous oxide and this material is preferred for use. Cuprous oxide is itself an exceptionally good insulator of electricity. Additionally, when reduced, as by treatment with an acid, the cuprous oxide may be changed to metallic copper to initially form the conducting portion of the desired printed circuit design which may then be further built up by electroless deposition by immersion or otherwise treating with the electroless copper depositing baths to be disclosed.

The catalytic compositions of the present invention may take a variety of forms.

For example, the insulating base members contemplated for use are most frequently formed of resinous material. When this is the case, the active agent disclosed herein, and especially copper oxide, in finely divided form, may be incorporated into the resin by milling, calendering, or other conventional methods after which the resin is set to form the base.

Alternatively, a thin film or strip of unpolymerized resin having particles of the active agent suspended therein might be laminated to a resinous insulated base and cured thereon. In this embodiment, the insulating base could be a resin impregnated laminate of paper or cloth sheets or Fiberglas.

In the preferred embodiment an ink comprising an adhesive resinous material having dispersed therein finely divided particles of the catalytic agent is printed on the surface of an insulating support and cured thereon.

Regardless of the manner in which it is incorporated in or on the base material, the catalytic agent is present in a finely divided form and preferably passes 200 mesh,

U.S. Standard Sieve Series. Ordinarily from a small fraction of 1% to about 80% of the active agent is admixed with adhesive resinous material to form the catalytic composition, but this concentration will depend to a large extent upon the materials used, and upon the time in which the catalytic compositions are allowed to remain in the electroless plating bath.

The resins into which the particles of the active material are dispersed preferably comprise, in combination, a thermosetting resin and a flexible adhesive resin. Typical of the thermosetting resins may be mentioned oil soluble phenolic type resins, such as fusible copolymers of phenol, resorcinol, a cresol, or a xylenol with an aldehyde or with furfural. Also may be mentioned the polyester resins, which are well known in the art and are prepared by reacting dicarboxylic compounds with dihydric alcohols, for example, by the reaction of phthalic or maleic anhydride with mono-, di- or polyethylene glycols. The polyester resins are ordinarily dissolved in styrene monomer and cross-linked by reaction with the styrene. As the thermosetting resin may also be mentioned epoxy resins, such as the reaction product of epichlorohydrin with bisphenol A.

Typical of the flexible adhesive resins are the epoxy resins, polyvinyl acetal resins, polyvinyl alcohol, polyvinyl acetate, and the like. Also as the adhesive resins may be mentioned chlorinated rubber and butadiene acrylonitrile copolymers.

The adhesive resins of the type described have appended thereto polar groups, such as nitrile, epoxide, acetal, and hydroxyl groups. Such adhesive resins copolymerize with and plasticize the thermosetting resins, and impart good adhesive characteristics through the action of the polar groups.

The thermosetting resin portion of the composition is required in order to afford resistance to heat upon soldering, and also to protect against decomposition when subjected to the electroless copper bath. A thermosetting resin alone, however, will not ordinarily have adequate tackiness or sufficient flexibility to resist heat shock; and would have negligent resistance to peeling of long conductor patterns from the surface. Admixture of adhesive resins such as those disclosed overcome the deficiencies of the thermosetting resins, and together, the thermosetting and adhesive resins provide an especially suitable composition for carrying the catalytic agents and for adhesively binding them to the base.

Particularly suitable for use as the adhesive resin for certain substrates is a combination of a phenolic type resin and an epoxy resin. The most common epoxy resins for use in the resinous composition are copolymers of epichlorohydrin (1-chloro-2,3-epoxy propane) with bisphenol A (2,2-p-hydroxy phenyl propane) which have melting points within the range of 20° F. to 375° F. and molecular weights of about 350 to 15,000.

Although epichlorohydrin is the most important organic epoxide employed in the formation of the epoxy resins, other epoxides such as, for example, 1,2,3,4-di-epoxy butane may be used. Similarly, epoxy resins derived from phenols other than bisphenol A are suitable for use. Such resins include, for example, the reaction product of epichlorohydrin with resorcinol, with phenols derived from cashew nut oils, with hydroquinone, with 1,5-dihydroxy naphthalene or with 2,2,5,5-tetrakis-(4-hydroxy phenyl) hexane. Phenolic intermediates of the resol type, hydrazines and sulfonamides, such as, for example, 2,4-toluene disulfonamide, may also be used for reaction with an organic epoxide to produce epoxy resins suitable for use. Aliphatic epoxy resins are also suitable. Such resins are, for example, the reaction product of epichlorohydrin with glycerol, with ethylene glycol or with pentaerythritol.

The phenolic type resin may be a copolymer of a phenol, resorcinol, a cresol or a xylenol with an aldehyde or with furfural. Thus, it may be a copolymer of

phenol or a substituted phenol with formaldehyde or a formaldehyde-yielding material, such as, paraformaldehyde or hexamethylene tetra-amine. The phenolic resin is preferably of the oil soluble type. As examples of thermosetting phenolic type resins which may be used may be mentioned copolymers of formaldehyde with p-cresol, p-ethyl phenol, p-tert butyl phenol, p-tert amyl phenol, p-tert octyl phenol, p-phenyl phenol, di-isobutyl phenol, or a "bisphenol," such as 4,4-isopropylidene diphenol or 2,2-bis(p-hydroxy phenyl) propane. It may be of the modified type, such as, for example, one which has been modified with copal or rosin to cause it to be oil soluble.

The phenolic type resins are, themselves, curing agents for the epoxy resins, and even those which are, themselves, permanently fusible form a tough, adherent film in combination with an epoxy resin which is probably the result of a cross-linking between the epoxy resin and the phenolic type resin. However, the resinous compositions may contain an additional curing agent. This curing agent may be another resin, such as, for example, a polyamide resin or a melamine-formaldehyde resin, or it may be, for example, a dibasic acid, such as, for example, phthalic anhydride, an amine, such as, for example triethanolamine, diethylene triamine or metaphenylene diamine, or an amide, such as, for example, dicyandiamide.

When using a thermosetting type of phenolic resin, a curing agent for the phenolic, such as, for example, one of the amines mentioned hereinabove as a curing agent for epoxy resin may be employed.

The active agent, it should be clear, is incorporated into the resinous compositions in such a way that the agent is dispersed throughout the resin, and present in the resin, upon solidification, at numerous individual sites. Because of this dispersion, the particles of the receptive agents are not in contact with one another and accordingly, the catalytic compositions disclosed herein are non-conducting. Of course, when the active agent is itself non-conducting, such as cuprous oxide, or titanous oxide, this factor is not important. When metals such as copper, iron, and so forth, are employed as the active agent, however, the dispersion of the active particles throughout the resin becomes important. Were conducting particles to be incorporated into the catalytic compositions in such a manner that they were in intimate contact with one another, it would be impossible to prepare printed circuits from such compositions using the so-called reverse method. In this method, the catalytic composition would be adhered to the over-all surface of the base material or the base material would itself constitute the catalytic composition, and selected portions thereof would then be masked, leaving exposed the conductor pattern. The base would then be immersed in the electroless copper bath to deposit copper on the exposed areas. Were the catalytic composition employed conductive, leakage would occur between the lines of the conductor pattern through the catalytic composition. Obviously, such a situation could not be tolerated.

When large amounts of the active agent are employed, as compared to the resin, relatively small amounts of resin bind the uppermost or surface particles of the active agent. Accordingly, electroless copper can readily deposit on the active agent on the surface. When small amounts of the active agent are employed in comparison to the resin, e.g., 0.25 to 10% by weight, it may be that the active agent at the surface of the catalytic composition will be completely coated by the resinous material. In this situation, it may be necessary to abrade the surface so that the particles will be exposed to the electroless plating bath. If, in this situation no abrasion is used, it will be necessary to expose the surface to the electroless plating bath for several hours before the initial copper deposit will form.

When copper oxide is used, it is preferable to activate the cuprous oxide by treatment with an acid, to convert at least a portion of the cuprous oxide particles at the

surface of the ink to copper. Preferred for use is sulfuric acid. Other reducing agents which are acceptable include aqueous solutions of phosphoric acid, acetic acid, sulfuric acid, hydrofluoric acid, dithionates, hypophosphites, and the like. Nitric acid may also be used but it is not quite as desirable as the others since it dissolves the copper formed at a rather high rate. Alkaline formaldehyde solutions including the electroless copper baths disclosed herein will also reduce the cuprous oxide.

Among the wide variety of adhesives which may be used when it is desired to prepare the catalytic compositions in the form of inks are those compositions disclosed in U.S. Patent Nos. 2,532,374 and 2,758,953. In this embodiment, the receptive agent, as will be clear, is imparted into the adhesive base in such a way that the receptive agent is dispersed throughout the base medium, and present in the base medium at numerous individual sites.

Typical examples of catalytic inks suitable for use in printing conductor patterns on an insulating base are given below:

EXAMPLE 1

	Xylene -----	G.
	Diacetone alcohol -----	50
25	Parlon 10 cps. -----	75
	Phenol-formaldehyde (oil soluble) -----	50
	Butadiene-acrylonitrile rubber -----	10
	Cab-O-Sil -----	20
	Cuprous oxide -----	3
30		70

EXAMPLE 2

	Butadiene acrylonitrile rubber -----	15.5
35	Diacetone alcohol -----	72
	Nitromethane -----	72
	Phenol-formaldehyde resin (oil soluble) -----	7.5
	Cab-O-Sil -----	4
	Ethanol -----	3
40	Parlon 10 cps. -----	10
	Xylene -----	50
	Cuprous oxide -----	80

EXAMPLE 3

45	Butadiene acrylonitrile rubber -----	15.5
	Diacetone alcohol -----	50
	Nitromethane -----	50
	Phenol-formaldehyde resin (oil soluble) -----	7.5
50	Parlon 10 cps. -----	3
	Toluene -----	20
	Cab-O-Sil -----	3
	Ethanol -----	3
55	Cuprous oxide -----	60

EXAMPLE 4

	Butadiene acrylonitrile rubber -----	15.5
	Diacetone alcohol -----	50
60	Nitromethane -----	50
	Phenol-formaldehyde resin (oil soluble) -----	7.5
	Cab-O-Sil -----	3
	Ethanol -----	3
65	Cuprous oxide -----	60

EXAMPLE 5

	Toluene -----	50
	Diacetone alcohol -----	50
70	Butadiene acrylonitrile rubber -----	10.5
	Phenol-formaldehyde resin (oil-soluble) -----	7.5
	Parlon 10 cps. -----	5
	Ethanol -----	5
	Cab-O-Sil -----	6
75	Cuprous oxide -----	50

EXAMPLE 6

Epoxy resin -----	G. 15
Butadiene acrylonitrile rubber -----	15
Diacetone alcohol -----	50
Toluene -----	50
Phenol-formaldehyde resin (oil soluble) -----	11
Cuprous oxide -----	60

In the above examples, Parlon is a chlorinated rubber from Hercules Powder Company. The epoxy resin of Example 6 is DER 332, sold by Dow Chemical Company, and is the reaction product of epichlorohydrin and bisphenol A. It has an epoxy equivalent of 173 to 179, an average molecular weight of 340 to 350 and a viscosity at 25° C. of 3600 to 6400. Cab-O-Sil is a tradename for silica aerogel.

To prepare the coating compositions or inks disclosed in Examples 1 to 6, the resins are dissolved in the solvents and milled with the pigments on a three roll mill.

The viscosity of compositions having the formulae of Examples 1 to 6 will ordinarily vary between about 5 and 100 poises at 20° C.

The catalytic inks may be applied to the panel in any convenient manner. For example, when a direct process for making printed circuits is employed, the circuit pattern of the ink may be imposed on the insulating base by screen printing or offset printing techniques. When the reverse process is employed, the insulating base may be coated with the catalytic ink, as by dipping, spraying, calendering, and the like, and then portions thereof masked to leave exposed the conductor pattern. When the catalytic inks are used to produce plated through holes, the ink may be drawn into the holes by vacuum. Alternatively, the pierced panels may be dipped into the inks, and then vibrated to remove excess ink from the holes.

After treatment of the panel with the catalytic ink, the adhesive base of the ink may be partially or fully cured by heating, thereby firmly bonding the adhesive ink with its contained receptive agent to the insulating base member.

The insulating base materials used to make the printed circuits must be able to withstand the temperatures which will be encountered in processing and in use. Preferable for use as insulating base materials are sheets of ceramic, phenol-formaldehyde, melamine-urea, vinyl acetate-chloride copolymer, rubber, epoxy resin polymers, epoxy impregnated Fiberglas, and the like.

After curing, the catalytic ink may be lightly abraded by rubbing its surface with steel wool, sand paper or other abrasive material so that the receptive particles which make up the active sites are exposed. As indicated hereinabove, this step is not always necessary and depends to a large extent upon the exact nature of the adhesive composition employed in the ink and upon the concentration of the receptive particles in the ink.

Electroless plating baths preferred for use in the present invention consist essentially of a soluble copper salt (e.g., copper sulfate, cupric chloride, cupric nitrate, copper gluconate, cupric acetate, and the like); a complexing agent for the cupric ions (e.g., Rochelle salts; ethylene diamine tetraacetic acid and its sodium salt; nitrolotriacetic acid and salts thereof; N-hydroxyethylethylenediamine triacetate; triethanolamine; sugar, including sucrose, dextrose, lactose, levulose or maltose; mannitol; sorbitol gluconic acid and the like; an alkali or alkaline earth metal hydroxide, such as sodium or potassium hydroxide; an active reducing agent such as formaldehyde; and a small amount of a complexing agent for cuprous ion, such as cyanide salts, e.g., sodium and potassium cyanide, acrylonitrile, lactonitrile, glyconitrile, thiourea, allyl alcohol, and ethylene. Preferred for use as the complexing agent for cuprous ion are the cyanide salts, such as sodium and potassium cyanide, acrylonitrile, lactonitrile, and glyconitrile.

The quantities of the various ingredients in the bath are subject to wide variation, within certain ranges which may be defined as follows:

- Copper salt from 0.5 g. to saturated solution (0.002 to .15 mol. or more).
- Alkali metal hydroxide to give pH 10.5 to 14.
- Formaldehyde 0.06 to 3.4 mol.
- Complexing agent for cupric ion 0.5 to 2.5 times moles of copper.
- Complexing agent for cuprous ion (0.00002 mol. to 0.06 mol.).
- Water—sufficient to make 1 liter.

The ratio of the copper salt to the complexing agent for cupric ion should be such that there are from 0.5 to 2.5 as many moles of cupric complexing agent as of copper, e.g., 5 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ requires from 2.5 to 8.5 grams of Rochelle salts.

Sodium hydroxide and sodium cyanide are preferred over the corresponding more costly potassium and other alkali metal salts, which are of greater molecular weight.

Rochelle salts, the sodium salts (mono-, di-, tri-, and tetrasodium salts) of ethylenediaminetetraacetic acid, nitrilotriacetic acid and its alkali salts, gluconic acid, gluconates, and triethanolamine are preferred as cupric ion complexing agents, but commercially available gluconolactone and modified-ethylenediamineacetates are also useful, and in certain instances give even better results than the pure sodium ethylenediaminetetraacetates. One such material is N-hydroxyethylethylenediaminetriacetate.

Cupric sulfate is preferred as the copper salt, but other soluble copper salts may be used, such as the nitrate, chloride and acetate.

In considering the general formulae for the electroless copper baths and the specific working formulae which are set forth below, it should be understood, that as the baths are used up in plating, the cupric salt, and the formaldehyde reducing agent may be replenished from time to time, and also that it may be advisable to monitor the pH and cuprous ion complexing agent content of the bath, and to adjust these to their optimum value as the bath is used.

The baths are ordinarily used at slightly elevated temperatures, such as from 35° to 65° C. although many of them may be used at even higher temperatures. As the temperature is increased, it is usual to find that the rate of plating is increased, and that the ductility of the deposit is increased to a slight extent, but the temperature is not highly critical, and within the usual operating range, excellent deposits are produced which exhibit greatly improved properties over those obtained with conventional baths.

With electroless copper plating baths used herein, the efficiency of copper recovered by electroless deposition from the bath often exceeds 90%, which is much greater than has heretofore been observed in working with conventional baths.

The cuprous ion complexing agent in the bath is an important feature and serves to prevent or minimize the formation of cuprous oxide in the bath, and also appears to inhibit the formation of resulting hydrogen in the electroless deposited metal. Without the cuprous ion complexing agent, e.g., cyanide and the like, the bath has been found to be unsatisfactory as a stable plating solution, and the electroless copper deposit has been found to be smudgy and of a poor appearance on the surface opposite the adhering base. Additionally, it has been discovered that without the cuprous ion complexing agent, a ductile deposit of electroless copper is not obtained.

The baths to be described herein will ordinarily deposit a coating of electroless copper of a thickness of about 1 mil, within between about 10 and 100 hours, depending on the composition, pH, temperature, and related factors.

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Examples of the electroless copper depositing baths suitable for use will now be described.

EXAMPLE 7

	Moles/l.
Copper sulfate	0.03
Sodium hydroxide	0.125
Sodium cyanide	0.0004
Formaldehyde	0.08
Tetrasodium ethylene-diaminetetraacetate	0.036
Water, remainder.	

This bath is preferably operated at a temperature of about 55° C., and will deposit a coating of ductile electroless copper about 1 mil thick in about 51 hours.

Other examples of suitable baths are as follows:

EXAMPLE 8

	Moles/l.
Copper sulfate	0.02
NaOH	0.05
NaCN	0.0002
Trisodium N-hydroxyethyl-ethylenediaminetriacetate	0.032
Formaldehyde	0.08
Water, remainder.	

This bath is preferably operated at a temperature of about 56° C., and will deposit a coating of ductile electroless copper about 1 mil thick in about 21 hours.

EXAMPLE 9

	Moles/l.
Copper sulfate	0.02
NaOH	0.125
NaCN	0.0002
HCHO	0.47
Rochelle salt	0.0425
Water, remainder.	

EXAMPLE 10

	Moles/l.
Copper sulfate	0.04
NaOH	0.19
NaCN	0.0002
Rochelle salt	0.0425
HCHO	0.47
Water, remainder.	

EXAMPLE 11

	Moles/l.
Copper sulfate	0.04
NaOH	0.19
NaCN	0.0006
HCHO	0.47
Rochelle salt	0.0425
Water, remainder.	

EXAMPLE 12

	Moles/l.
Copper sulfate	0.04
Sodium hydroxide	0.19
NaCN	0.0002
HCHO	0.47
Rochelle salt	0.064
Water, remainder.	

EXAMPLE 13

	Moles/l.
Copper sulfate	0.02
NaOH	0.125
NaCN	0.0002
HCHO	0.40
Sodium citrate	0.051
Water, remainder.	

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EXAMPLE 14

	Moles/l.
Copper sulfate	0.02
NaOH	0.05
NaCN	0.0002
HCHO	0.1
Trisodium N-hydroxy ethylenediaminetriacetate	0.024
Water, remainder.	

The following examples are illustrative of the improved methods of making printed circuits according to the teachings contained herein.

EXAMPLE 15

15 An insulating base is formed by uniformly mixing 155 grams of Ciba 6005 which is the reaction product of bisphenol A and epichlorohydrin which has a viscosity of 4500 centipoises and an epoxy equivalent of 175 and adding to it an equal weight of cuprous oxide which passes 20 200 mesh and milling with the pulverulent copper oxide particles for 1 to 2 minutes, which makes for a mixture which is relatively uniform. This uniform mixture is ready for immediate use or may be set aside for later use. It has an amine hardener, in this case 70 grams of diethylene triamine blended with it by constant turning, 25 cutting and rubbing for about 2 minutes. It is then transferred to a mold by means of which it is given the shape desired. Heat may be applied to speed setting of the epoxy resin loaded with cuprous oxide particles so that the reaction is complete in a period of about one hour.

30 One surface of the insulating base thus formed is provided with a resist, portions of which have been removed, said portions masking out the circuit design which it is desired to form. An aqueous solution of 30° Baumé 35 sulfuric acid is then applied to the resist covered surface. The strength of the acid is not particularly critical and acid strengths of from 5° to 40° Baumé have proven quite acceptable. The acid is allowed to remain in contact with the resist covered surface for 10 minutes. 40 Contact of from 5 to 15 minutes is the usual period of time in which the cuprous oxide particles which are unprotected by the resist are reacted upon by the acid and converted to metallic copper. The acid is then removed by a thorough rinsing and the insulating base is then immersed 45 in the electroless copper bath of Example 7 for about 51 hours. A uniform, adherent, bright, ductile copper deposit about 0.001 inch thick was built up during this period of time. The deposit was tenaciously adhered to the base and could only be removed by scraping. The deposit 50 could be readily soldered, both by dipping in a hot solder bath, and by hand soldering.

EXAMPLE 16

55 Since only the surface portion of the insulating base is acted upon during the contact with the acid it has proven desirable in some cases to take a cuprous oxide loaded resin and coat the surface of an insulating support with a lamina of such a composition and cure it thereon. A coating of epoxy resin-cuprous oxide as described in Example 15 is applied to a clean urea-formaldehyde resin support to a depth of about $\frac{3}{16}$ of an inch and cured thereon. This depth may be varied on either side of that 60 used here but $\frac{1}{16}$ of an inch is the most useful for any practical purpose. After curing this lamina thereby bonding it to the insulating base substance, the other steps of the process, i.e., masking, developing with acid and electrolessly plating, are carried out as in Example 15, and comparable results are obtained.

EXAMPLE 17

70 Example 15 was repeated with the exception that the molded, cuprous oxide loaded insulating base, following formation, is pierced to define apertures, holes or cross-over points between the top and bottom surfaces of the 75

base. The apertures could be formed by drilling or cutting. When treated in the acid and then immersed in the electroless copper depositing bath, electroless copper deposits on the lateral sides surrounding the holes as well as on the circuit design. As will readily be appreciated, this technique affords an extremely simple and facile method of making printed circuits with plated through holes.

The cuprous oxide loaded base of Example 15 also permits formation of printed circuits in a solid block of insulating material, as will be clear from the following examples.

EXAMPLE 18

A cylindrical block of cuprous oxide loaded resin was prepared following the procedure of Example 15. The surfaces of the cylindrical block are then covered completely with a resist. Holes are then drilled into the cylindrical block to form a pattern of interconnecting channels. Drilling the holes exposes the catalytic agent at myriad individual sites on the walls defining the holes. The cylindrical block is then treated with acid and immersed in the electroless copper bath, as described in Example 15. An adherent uniform, bright, ductile copper deposit is thereby formed on the lateral walls of the holes to form a printed circuit which is entirely encased in the cylindrical block.

If desired, of course, a circuit pattern could also be imposed on the exterior surfaces of the block. The conducting pattern on the surface could connect or not connect with the circuit in the interior of the block.

The importance of such a technique in forming micro-miniature circuits will readily be apparent to those skilled in the art.

In Examples 17 and 18, the solid block of material used to form the printed circuit could of course be any geometrical shape, such as spherical, tetragonal, hexagonal and the like.

EXAMPLE 19

Another variation of this invention is the provision of cuprous oxide in an adhesive resin-based ink which may be printed directly on an insulating base support such as epoxy impregnated Fiberglas. A suitable ink formulation for use in this embodiment is made up by weight as follows:

	Parts
Phenol-formaldehyde resin (alcohol soluble) -----	60
Polyvinyl butyral resin -----	40
Ethanol -----	100
Cuprous oxide (powder, pass 200 mesh) -----	150
Powdered silica (methyl isobutyl ketone) sufficient to adjust viscosity to about 200 poises.	

The resin-based ink circuit thus outlined is cured, bonding it to the resin insulating base. The cuprous oxide particles are reduced to metallic copper by means of contacting the cured resin-based ink containing cuprous oxide particles with an acid and building up the circuit in the same manner as in Example 15.

If plated through holes are desired, these may be achieved by piercing the insulating base support prior to or following printing, and coating the lateral walls surrounding the holes with the catalytic ink, and curing. The panel is then treated with the acid and then with the electroless copper bath to deposit copper on the conductor pattern and on the lateral walls surrounding the holes.

EXAMPLE 20

An adhesive containing a small amount of copper oxide (Cu_2O) is prepared as follows:

	Parts by wt.
Butadiene-acrylonitrile copolymer ¹ -----	23
Phenol-formaldehyde resin ² -----	10
Zirconium silicate -----	107
Silica (20) -----	4

Cuprous oxide -----	0.5
Isophorone -----	90
Xylene -----	31

¹ Medium high acrylonitrile content.

² Combination of 5 parts oil soluble, heat reactive, solid resin, M.P. 144-162° F. and 5 parts alcohol soluble, oil soluble, heat reactive solid resin.

The rubber is dissolved in part of the solvents and the phenolic resin dissolved separately in the rest of the solvents. The two solutions, cuprous oxide and the pigments are blended in a three roll paint mill. The circuit design is screen printed with the resulting ink on an epoxy-impregnated Fiberglas laminate and cured. The cured print of the circuit is immersed in 20° Baumé sulfuric acid solution for 10 minutes. It is then removed, washed free of sulfuric acid and immersed in the electroless plating bath described hereinabove. Again, plated through holes may be formed, if desired, using the procedure of Example 19.

EXAMPLE 21

A molding composition containing 10% cuprous oxide is prepared as follows:

	Parts
(1) Epoxy resin (reaction product of bisphenol A and epichlorohydrin having an epoxide equivalent of 180 to 200 and an average molecular weight of 350 to 400) -----	30
(2) Cuprous oxide -----	10
(3) Polyamide resin (having an amine value of 210 to 230, the condensation product of dimerized or trimerized fatty acids with aryl or alkyl polyamines) -----	60
(4) Zirconium silicate -----	97
(5) Silica (20) -----	4

The epoxy resin, cuprous oxide and pigments are blended together in a three roll paint mill, and the polyamide resin was warmed until readily workable and blended with the mixture from the mill by constant turning, cutting and rubbing for 5 minutes. The mix was cast in a mold and cured at 250° F. for 45 minutes. The fabrication of the printed circuit was carried out as in Example 1.

EXAMPLE 22

Examples 15 to 21 are repeated with comparable results using finely divided particles of titanium, aluminum, copper, iron, cobalt, zinc, and titanous oxide as the catalytic agent. With these agents, the acid treatment was not necessary. Best results were achieved when the catalytic composition was slightly abraded prior to exposure to the electroless copper bath.

EXAMPLE 23

Holes are drilled in a cylindrical block of acrylic resin having a diameter of $\frac{3}{4}$ inch and a height of 1 inch. The holes are drilled at various angles and various directions so that they interconnect each other at selected positions, as shown, for example, in FIGURE 4.

The holes are cleaned by treating with a mild alkaline cleaner, and then the holes are coated with the catalytic ink of Example 1. Residual ink is removed from the surface of the cylinder. The cylinder is then treated with acid and immersed in the electroless copper depositing bath. An adherent, bright, ductile copper deposit is formed on lateral walls surrounding the holes to form a printed circuit completely encapsulated with the cylinder of acrylic resin.

The particular amounts of catalytic agent shown as specific examples herein are operable, although the preferred amounts for obtaining a rapid electroless deposition while using a reasonable amount of catalytic agent is between 10 and 20% by weight. The initial copper deposition obtained with these amounts occurs within about

2 to 10 minutes after immersion in the electroless plating bath.

The following figures are included to illustrate the major embodiments of the catalytic compositions disclosed herein.

FIGURE 1 shows an insulating base 1 which has randomly distributed particles of cuprous oxide 2;

FIGURE 2 shows an insulating support 3 to which there has been laminated an insulating base 1 in which there is randomly distributed particles of cuprous oxide 2;

FIGURE 3 shows an insulating support 3 having applied on its surface particles of cuprous oxide 1 in the form of filler in an adhesive ink 4;

FIGURES 4, 4a and 4b show an embodiment of a printed circuit in which the printed circuit pattern 6 is formed in holes bored into a solid mass of an insulating material 8, as described in Example 24; and

FIGURE 4 is an isometric view of the circuit and FIGURE 4a is a cross sectional view showing how the interconnecting circuit pattern 6 comprising the electroless copper deposit 10 runs through the insulating material 8. FIGURE 4b is an enlarged cross sectional view of the conducting pattern of FIGURE 4a and depicts how the electroless deposited copper 10 is adhered to the catalytic composition 12 which in turn is bonded to the lateral wall of insulating material 8 defining the aperture 6.

The FIGURES 1 to 3 show intermediate products resulting from the carrying out of the methods described in the corresponding examples in the specification in that FIGURE 1 corresponds to Example 15, FIGURE 2 corresponds to Example 16 and FIGURE 3 corresponds to Example 19.

FIGURES 4, 4a and 4b are schematic illustrations of the printed circuit produced according to the teachings of Example 23.

As is clear from the foregoing examples, the base materials on which the metal is deposited are capable of wide variation in composition and configuration. Among base materials to which the catalytic composition may be adhered may be mentioned impregnated laminates of paper or cloth, or even Fiberglas. The resin impregnant for such laminates include phenolics, epoxys, polyesters, and the like. When impregnated laminates are used, it is desirable to pre-coat the laminates with a smooth plastic film prior to adhering the catalytic composition.

As is also clear from the foregoing examples, the base materials may include molded plastic, such as molded epoxy resin, polyester resin, epoxy resin, and the like.

The base materials may even have incorporated therein the active agent for reception of the electroless copper deposit, as is clear from Example 15. In this embodiment, it is not necessary to separately adhere the catalytic composition to the base material, since the base material itself forms the blank from which printed circuits may be made directly.

Still other possible base materials include lightweight synthetic materials well known to the building trade, such as wallboard, Masonite, Transite, and the like. Also may be mentioned anodized aluminum which has been sealed in a manner well known in the art to render the anodized coating insulating.

Also suitable for use as the base material are plastic coated article is heated to fuse the coating. The particles or steel coated with a resin. Such plastic coated metals are well known in the art, and are commercially available. They may be prepared either by dip coating, spray coating, or flame coating metal substrates with a resin. Preferably, however, since smooth surfaces are desired, such metal resin coated laminates are prepared by fluidized bed techniques which are now well known in the art and described, for example, in U.S. Patent 3,028,251.

Suitable compositions for use in fluidized bed coating of a metal substrate with an insulating coating of a

plastic material comprise a mixture of fusible epoxy resin and a fusible phenolic type resin. The compositions are in the form of free-flowing powders, which are fusible at an elevated temperature below the temperature at which the resin will be decomposed during the formation of the coating by fusion. Compositions in which the epoxy resin varies from about 10 to about 90%, based upon the total weight of the two resins, are preferred. The coating composition may contain other types of resins in addition to epoxy resin and phenolic resin, such as, for example, a polyester resin, a polyamide resin, a melamine formaldehyde resin or a natural resin, such as copal or rosin.

In the fluidized bed coating technique, finely divided solid particles of the resin composition are fluidized in a stream of gas, such as air, and a pre-heated article to be coated immersed in the fluidized bed for suitable periods of time. Following removal from the bed, the coated article is heated to fuse the coating. The particles of resin in the fluidized bed will ordinarily range in size from about 5 to 600 mesh, United States Standard Sieve Series.

The following examples illustrate methods of forming printed circuits using plastic coated metal base materials.

EXAMPLE 24

Fifty parts, by weight, of an epoxy resin formed by the reaction of bisphenol A with epichlorohydrin and characterized by an epoxide equivalent (grams of resin containing one gram equivalent of epoxide) within the range of 1550 to 2000, an equivalent weight of 190, a melting point of 127° C. to 133° C. and a particle size less than 40 mesh, fifty parts, by weight, of a phenolic resin produced by the reaction of phenol with formaldehyde and characterized by a softening point of 180° F. to 220° F., a specific gravity of 1.2 and a particle size less than 40 mesh and two parts, by weight, of powdered silica having a particle size ranging from 1 micron to 7 microns were dry blended together.

A pierced and blanked aluminum plate having a thickness of 1/8 inch, a width of about 3 inches and a length of about 6 inches was heated to a temperature of 400° F. and while at that temperature immersed in a fluidized bed of the dry resin blend for a period of time ranging from 1/4 second to 2 seconds. Upon removal from the fluidized bed, the coated panel was maintained at a temperature of about 400° F. for a period of about 15 minutes to cure the coating which had been deposited thereon. Upon curing, the coating on the plate was found to vary from about 2 to 10 mils in thickness, depending upon the time of contact in the fluidized bed. The coating was semi-gloss transparent and showed the natural color of the aluminum.

The coating extended through the plurality of holes in the panel. These holes had an original diameter of about 50 mils.

The resulting plastic coated aluminum was screen printed with the catalytic ink described in Example 2 to form a conductor pattern. The catalytic ink circuit thus outlined was cured to firmly bond it to the base. The cuprous oxide particles in the catalytic ink were reduced to metallic copper by immersion in sulfuric acid following the procedure of Example 15. The panel was then immersed in the bath of Example 8 for a period of about 36 hours, thereby building up a printed circuit in the same manner as in the previous examples.

Following electroless copper deposition, the panel was post cured by heating for about 2 hours at 130° C.

In this embodiment, plated through holes may be readily formed by coating the lateral walls surrounding the holes with the catalytic ink prior to acid treatment and immersion in the electroless copper bath.

Example 24 is repeated with the exception that 20% by weight of cuprous oxide having a particle size of less than 200 mesh, U.S. Standard Sieve Series, based on the weight of the resin, was incorporated into the resinous composition prior to blending.

A pierced and blanked aluminum plate was anodized and coated with the resulting composition using the technique described in Example 24.

The plastic coating contained particles of cuprous oxide finely dispersed throughout. To form the printed circuit, the surface of the panel was coated with a masking composition which left exposed a conductor pattern and also the lateral walls surrounding the holes. The panel was then immersed in sulfuric acid having the strength of about 25% for about 5 to 15 minutes to reduce at least a portion of the cuprous oxide to copper in the exposed areas of the conductor pattern and in the holes. The panel was then immersed in the electroless copper plating bath of Example 9 for about 75 hours, at the end of which time a firmly adherent, ductile, and bright electroless copper deposit had built up on the conductor pattern and on the lateral walls surrounding the holes.

In this example, the holes in the aluminum panel were coated by the fluidized bed technique, so that the holes actually had cuprous oxide particles adhered to the lateral sides of the holes. The wall surrounding the holes, in other words, following activation of the cuprous oxide with the acid, contained sites catalytic to electroless copper deposition. Accordingly, when the panel was submerged in the electroless copper bath, the walls surrounding the holes also received a uniform adherent deposit of electroless copper.

As will be clear, the technique described in this example is suitable to make printed circuits on both sides of an insulating panel with plated through holes directly. Heretofore, great difficulty has been experienced in the trade in making plated through holes using electroless deposition techniques. The procedure outlined in Example 25 as well as certain of the other examples contained herein, represents a significant advancement in the art of making plated through holes.

If desired, special properties may be imparted to the copper conducting patterns produced as disclosed herein, as for example by depositing nickel, gold, silver, rhodium, and similar metals on the copper conducting pattern in whole or in part.

Typical nickel baths which may be used to deposit the additional metals are described in Brenner, Metal Finishing, 1954, pages 68 to 76, and comprise acidic aqueous solutions of a nickel salt, such as nickel chloride; an active chemical reducing agent for the nickel salt, such as a hypophosphite; and a complexing agent, such as carboxylic acid and salts thereof. Suitable electroless gold plating baths which may be used to deposit additional metal are disclosed in U.S. Patent 2,976,181, and contain a slightly water soluble gold salt, such as gold cyanide, a reducing agent for the gold salt, such as the hypophosphite ion, and a chelating or complexing agent, such as sodium and potassium cyanide. The hypophosphite ion may be introduced in the form of hypophosphorous acid and salts thereof, such as sodium, calcium and ammonium salts.

It should be clear from the foregoing examples that when the embodiment using the adhesive resin ink is employed, printed circuits may be made by employing either the direct or reverse printing technique. Also, following formation of the conductor pattern, the copper circuit can be dip soldered in whole or in part. If only portions of the circuit are to be dip soldered, a permanent or non-permanent solder mask may be used to coat the conductor pattern prior to dip soldering. Also, if desired, the conducting copper pattern, either in whole

or in part, may receive an additional coating of metal, such as gold, silver, rhodium and the like, to impart special properties to the circuit as a whole or designated portions thereof.

It should be also be clear from the foregoing that completed circuits with plated through holes can be readily and facily made according to the techniques disclosed herein, including modifications of such techniques which will be obvious to those skilled in the art.

The invention in its broader aspects is not limited to the specific steps, methods, compositions and improvements shown and described herein, but departures may be made within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

What is claimed:

1. A process for metallizing insulating base materials which comprises adhesively binding to surfaces of the base material an agent catalytic to the reception of electroless copper, and then immersing the base material in an alkaline electroless copper depositing bath comprising water, a water soluble cupric salt, a complexing agent for cupric ion, a reducing agent for cupric ion, and a complexing agent for cuprous ion, to thereby build up an adherent, ductile layer of electrolessly deposited copper at sites where the catalytic agent is exposed to the bath.

2. The process of claim 1 wherein the catalytic agent is finely divided cuprous oxide, and wherein the cuprous oxide is reduced at least in part to copper prior to immersion in the alkaline copper electroless deposition bath.

3. The process of claim 1 wherein the catalytic agent is adhesively bound to the surfaces of the base material by incorporating the catalytic agent into an adhesive resin ink, applying the ink to the base material, and then curing the ink.

4. The process of claim 1 wherein the catalytic agent is adhesively bound to the surface of the base material by forming a strip of a resin containing the catalytic agent and adhesively adhering the strip to the base material.

5. The process of claim 1 wherein the base material is a molded resin having the catalytic agent dispersed therein.

6. The process of claim 1 wherein the complexing agent for cuprous ion is a water soluble cyanide salt.

7. The process of claim 1 wherein the aqueous alkaline electroless copper depositing bath comprises: about 0.02 to 0.15 mol. per liter of a water soluble copper salt, about 0.06 to 3.4 mols. per liter of formaldehyde; about 0.5 to 2.5 times the mols of copper of a complexing agent for cupric ion; as the cuprous complexing agent, about 0.00002 to 0.06 mol. per liter of a water soluble cyanide compound; and enough of an alkali metal hydroxide to give a pH of about 10.5 to 14.

8. The process of claim 1 wherein, as the alkaline electroless copper depositing bath, there is used an alkaline solution which comprises water, a water soluble copper salt, a complexing agent for cupric ion, a reducing agent for cupric ion, and a small effective amount of a water soluble cyanide compound.

9. A method of forming printed circuits which comprises preparing a plastic laminate by molding an adhesive resinous composition having dispersed therein finely divided solid particles of an agent catalytic to the reception of electroless copper and selected from the group consisting of titanium, aluminum, copper, iron, cobalt, zinc, copper oxide and titanous oxide, including mixtures of the foregoing; masking a portion of the surface of the resulting plastic article to leave exposed a circuit design; and immersing the article in an alkaline electroless plating bath comprising water, a water soluble cupric salt, an alkali metal hydroxide, a complexing agent for cupric ion, formaldehyde, and a complexing agent for cuprous ion, to thereby build up an adherent ductile layer of electrolessly deposited copper at sites on the surface of the laminate where the catalytic agent is exposed to the bath.

10. A method of forming printed circuits which com-

prises preparing a molded, three-dimensional article of a plastic insulating material having uniformly dispersed throughout finely divided solid particles of an agent catalytic to the reception of electroless copper; establishing interconnecting channels inside of the article to define a circuit pattern and to expose myriad sites of the catalytic agent on the walls defining the channels; and immersing the article in an electroless copper bath comprising water, a water soluble copper salt, an alkali metal hydroxide, a complexing agent for cupric ion, formaldehyde, and a complexing agent for cuprous ion, to thereby build up an adherent layer of electrolessly deposited copper at the sites on the walls defining the channels where the catalytic agent is exposed to the bath.

11. A method of forming printed circuits which comprises coating at least selected areas of an insulating base material with an ink comprising an adhesive resin having dispersed therein an agent catalytic to the reception of electroless copper; and immersing the resulting insulating base material in an alkaline electroless copper bath comprising water, a water soluble cupric salt, a complexing agent for cupric ion, a reducing agent for cupric ion, and a complexing agent for cuprous ion, to thereby build up an adherent, ductile layer of electrolessly deposited copper at the sites where the catalytic agent is exposed to the bath.

12. The method of claim 11 wherein, as the alkaline electroless copper depositing bath, there is used an alkaline solution which comprises water, a water soluble copper salt, a complexing agent for cupric ion, a reducing agent for cupric ion, and a small effective amount of a water soluble cyanide compound.

13. The method of claim 11 wherein the ink comprises, in combination, a thermosetting resin which is a member selected from the group consisting of phenolic resins, polyester resins, epoxy resins, and mixtures of the foregoing; and an adhesive resin which is a member selected from the group consisting of epoxy resin, polyvinyl acetal resin, butadiene-acrylonitrile resin, chlorinated rubber, and mixtures of the foregoing.

14. A method of forming printed circuits which comprises providing interconnecting apertures in a solid insulating material of predetermined configuration; coating the lateral walls of the apertures with an adhesive resin ink having dispersed therein finely divided solid particles of an agent which is catalytic to the reception of an electroless copper deposit; curing the resin to adhesively bond the catalytic agent to the walls; and immersing the article in an aqueous alkaline solution comprising water, a water soluble cupric salt, an alkali metal hydroxide, a complexing agent for cupric ion, formaldehyde, and a complexing agent for cuprous ion, to thereby build up an adherent ductile layer of electrolessly deposited copper at the sites where the catalytic agent is exposed to the bath.

15. A process for making printed circuits which comprises providing holes in a metal plate at points defining cross-overs between the top and bottom surfaces of the plate; coating the surfaces of the plate including the walls surrounding the apertures with a film of an insulating resinous material by heating the plate and immersing it in a fluidized bed of finely divided particles of the resinous material; coating at least selected areas of the resulting panel with an ink comprising an adhesive resin base having dispersed therein at numerous individual sites finely divided particles of an agent catalytic to the reception of electroless copper; curing the ink to adhesively bond the catalytic agent to the base; and immersing the resulting panel in an alkaline electroless copper bath comprising water, a water soluble cupric salt, an alkali metal hydroxide, a complexing agent for cupric ion, formaldehyde, and a complexing agent for cuprous ion, to thereby build up an adherent, ductile layer of electrolessly deposited copper at the sites where the catalytic agent is exposed to the bath.

16. The process of claim 15 wherein the lateral walls of the panel surrounding the apertures are coated with said ink, and wherein a ductile copper deposit is built up on said walls when the panel is immersed in the alkaline electroless copper depositing bath.

17. A process for making printed circuits which comprises providing apertures in a metal plate at points defining cross-overs between the top and bottom surfaces of the plate; anodizing the plate to render it non-conducting; coating the surfaces of the anodized metal plate and the walls surrounding the apertures with a composition comprising an adhesive resin having dispersed throughout finely divided solid particles of an agent catalytic to the reception of electroless copper by heating the plate and immersing it in a fluidized bed of finely divided solid particles of the adhesive resin composition; masking selected portions of the surfaces of the resulting resin coated panel to leave exposed a conductor pattern; and immersing the resulting panel in an aqueous alkaline electroless depositing bath comprising water, a water soluble cupric salt, an alkali metal hydroxide, a complexing agent for cupric ion, formaldehyde, and a complexing agent for cuprous ion, to thereby build up an adherent layer of electrolessly deposited copper at the sites where the catalytic agent is exposed to the bath.

18. A process for simultaneously depositing and tenaciously adhering a layer of ductile electroless copper having a uniform thickness on an insulating substratum which comprises adhesively binding to surfaces of the insulating substratum an agent which is catalytic to the reception of electroless copper and then contacting the substratum with an alkaline aqueous electroless copper depositing solution comprising a water soluble copper salt, a complexing agent for cupric ion, a reducing agent for cupric ion, and a complexing agent for cuprous ion.

19. The process of claim 18 wherein the cuprous ion complexing agent is a water soluble cyanide compound.

20. The method of claim 18 wherein the reducing agent for cupric ion is formaldehyde.

21. The method of claim 18 wherein, as the alkaline electroless copper depositing bath, there is used an alkaline solution which comprises water, a water soluble copper salt, a complexing agent for cupric ion, a reducing agent for cupric ion, and a small effective amount of a water soluble cyanide compound.

22. A method of forming metallized assemblies comprising an insulating base having a relatively thin film of metal adhered to a portion thereof which comprises establishing a three-dimensional insulating base comprising as adhesive resinous composition having dispersed therein an agent catalytic to the reception of electroless copper, and exposing at least a portion of said insulating base to a stable alkaline electroless copper plating solution capable of forming a ductile electroless copper deposit and comprising a water soluble cupric salt, water, a complexing agent for cupric ion, a reducing agent for cupric ion, and a complexing agent for cuprous ion, to thereby build up an adherent layer of electrolessly deposited copper at sites on the surfaces of the insulating base where the catalytic agent is exposed to the bath.

23. The method of claim 22, wherein in the alkaline electroless copper plating solution, the reducing agent for cupric ion is formaldehyde, and wherein said solution contains a small effective amount of a water soluble cyanide compound.

24. A method of metallizing interior portions of a three-dimensional insulating base material, which comprises, establishing a three-dimensional insulating base of an adhesive resinous composition containing an agent catalytic to the reception of electroless copper and containing at least one open, interior channel, said adhesive resinous composition forming the surrounding wall of said channel; and immersing the resulting insulating base in an alkaline electroless copper plating solution capable of forming a ductile electroless copper deposit and com-

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prising water, a water soluble copper salt, a complexing agent for cupric ion, a reducing agent for cupric ion, and a complexing agent for cuprous ion, to thereby build up an adherent layer of electrolessly deposited copper on the wall of the adhesive resinous composition surrounding the channel wherever the catalytic agent dispersed therein is exposed to the bath.

25. The method of claim 24, wherein in the alkaline electroless copper plating solution, the reducing agent for cupric ion is formaldehyde and wherein said solution contains a small effective amount of a water soluble cyanide compound.

26. A method of making printed circuits which comprises establishing a molded insulating base comprising an adhesive resinous composition containing an agent catalytic to the reception of electroless copper; masking a portion of the surface of the resulting insulating base to leave exposed a circuit design; and immersing the resulting base in an alkaline electroless copper plating bath capable of forming a ductile electroless copper deposit comprising water, a water soluble cupric salt, a complexing agent for cupric ion, a reducing agent for cupric ion, and a complexing agent for cuprous ion, to thereby build up an adherent layer of electrolessly deposited copper on the exposed circuit design.

27. The method of claim 26, wherein in the alkaline electroless copper plating solution, the reducing agent for cupric ion is formaldehyde, and wherein said solution contains a small effective amount of a water soluble cyanide compound.

28. A method of forming printed circuits which comprises establishing a three-dimensional insulating base comprising a resinous composition containing an agent catalytic to the reception of electroless copper, said base having at least one interior channel defining at least a portion of a circuit pattern; said channel being surrounded by a wall of said resinous composition; and immersing the base in a stable alkaline electroless copper bath comprising water, a water soluble copper salt, a complexing agent for cupric ion, and a reducing agent for cupric ion, to thereby build up an adherent layer of electrolessly deposited copper at sites on the wall of the channel where the catalytic agent is exposed to the bath.

29. The method of claim 28 wherein in the electroless copper plating solution, the reducing agent for cupric ion is formaldehyde, and wherein the copper plating solution comprises a small effective amount of a water soluble cyanide compound.

30. A method for making printed circuits which comprises providing holes in a resinous insulating base material said holes defining cross-overs between the top and bottom surfaces of said base, coating at least a selected area of the resulting base with an ink comprising an adhesive resinous composition containing an agent catalytic to the reception of electroless copper, curing the ink to adhesively bond the catalytic agent to the base and immersing the resulting panel in an alkaline electroless copper plating solution capable of forming a ductile electroless copper deposit and comprising water, a water soluble copper salt, a complexing agent for cupric ion, a reducing agent for cupric ion and a complexing agent for cuprous ion.

31. The method of claim 30, wherein in the alkaline electroless copper plating solution the reducing agent for cupric ion is formaldehyde and wherein said solution contains a small effective amount of a water soluble cyanide compound.

32. A method of making printed circuits which comprises providing interconnecting apertures in a solid insulating resinous base material, coating the lateral walls of the apertures with an adhesive resinous composition containing an agent catalytic to the reception of electroless copper, curing the resin to adhesively bond the resinous catalytic agent to the resinous base, and immersing the article in an aqueous alkaline electroless copper plat-

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ing solution capable of forming a ductile electroless copper deposit and comprising water, a water soluble copper salt, a complexing agent for cupric ion, a reducing agent for cupric ion, and a complexing agent for the cuprous ion.

33. The method of claim 32, wherein in the alkaline electroless copper plating solution the reducing agent for cupric ion is formaldehyde and wherein said solution contains a small effective amount of a water soluble cyanide compound.

34. A method of making printed circuits which comprises providing apertures in a metal plate at points defining cross-overs between the top and bottom surfaces of the plate, coating the surfaces of the plate including the walls surrounding the apertures with a film of an insulating resinous material, coating at least selected areas of the resulting panel with an adhesive resinous composition containing an agent catalytic to the reception of electroless copper, curing the resulting catalytic agent to adhesively bond the catalytic agent to the base, and immersing the resulting panel in an alkaline electroless copper plating solution capable of forming a ductile electroless copper deposit and comprising water, a water soluble copper salt, a complexing agent for cupric ion, a reducing agent for cupric ion, and a complexing agent for the cuprous ion.

35. The method of claim 34, wherein in the alkaline electroless copper plating solution the reducing agent for cupric ion is formaldehyde and wherein said solution contains a small effective amount of a water soluble cyanide compound.

36. A method for making printed circuits which comprises providing apertures in a metal plate at points defining cross-overs between the top and bottom surfaces of the plate, coating the surfaces of the plate with a non-conducting material including the walls surrounding the apertures, said non-conducting material comprising an adhesive resinous composition containing an agent catalytic to the reception of electroless copper, masking selected portions of the surfaces of the resinous coated panel to leave exposed a conductor pattern, immersing the resulting panel in an alkaline electroless copper plating solution capable of forming a ductile electroless copper deposit and comprising water, a water soluble copper salt, a complexing agent for cupric ion, a reducing agent for cupric ion and a complexing agent for cuprous ion.

37. The method of claim 36, wherein in the alkaline electroless copper plating solution the reducing agent for cupric ion is formaldehyde and wherein said solution contains a small effective amount of a water soluble cyanide compound.

38. The process for making printed circuits which comprises providing apertures in a metal plate at points defining cross-overs between the top and bottom surfaces of the plate; coating the surfaces of the plate, including the walls surrounding the apertures with a film of an insulating resinous material comprising an adhesive resin base having dispersed therein at numerous individual sites finely divided particles of an agent catalytic to the reception of electroless copper by heating the plate and immersing it in a fluidized bed of finely divided particles of said adhesive resinous material curing said adhesive resinous material to adhesively bond said resinous material and catalytic agent to said plate and immersing the resulting panel in an electroless copper bath comprising water, a water soluble cupric salt, an alkali metal hydroxide, a complexing agent for cupric ion, a reducing agent for the cupric ion and a complexing agent for the cuprous ion to thereby build up an adherent ductile layer of electrolessly deposited copper on the sites where the catalytic agent is exposed to the bath.

39. The process of claim 38, wherein selected portions of the surfaces of the resulting resin coated panel are masked to leave exposed a conductor pattern and subse-

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quently immersing the masked panel in said electroless depositing bath.

40. A process for making printed circuits which comprise providing holes in an insulating base at points defining cross-overs between the top and bottom surfaces of the base, said insulating base containing dispersed therein an agent which is catalytic to the reception of electroless copper deposit; coating said base with a resist material leaving exposed those areas defining the desired circuit pattern and said cross-overs; and immersing said base in an electroless copper deposit bath which comprises a water soluble salt, a complexing agent for cupric ion, a complexing agent for cuprous ion and a reducing agent for cupric ion.

41. The process of claim 40, wherein said catalytic agent comprises solid particles of finely divided catalytic material.

42. The process of claim 41, wherein said catalytic agent comprises finely divided solid particles of copper oxide.

43. A process for making printed circuits which comprises putting holes in an insulating base at points defining cross-overs between the top and bottom surfaces of the base, said base containing dispersed therein an agent which is catalytic to the reception of electroless copper deposit; coating at least a selected area of one of the top and bottom surfaces of said base with an adhesive resin ink having dispersed therein finely divided solid particles of an agent which is catalytic to the reception of an electroless copper deposit; and immersing the resulting panel in an alkaline electroless copper plating solution capable of forming a ductile electroless copper deposit and comprising water, a water soluble copper salt, a complexing agent for cupric ion, a reducing agent for cupric ion and a complexing agent for cuprous ion.

44. The process of claim 43, wherein the top and bottom surfaces of said panel are coated with said ad-

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hesive resin ink, said ink is cured to adhesively bond the catalytic agent to said base, and coating selected areas of said top and bottom surfaces of said panel with a resist material leaving exposed those areas defining the desired circuit pattern and said cross-overs.

45. The process of claim 43, wherein the top and bottom surfaces of said panel are coated with a resist material and at least a selected area of said resist material is coated with said adhesive resin ink in a pattern defining the desired circuit configuration and curing the ink to adhesively bond the catalytic agent to the base.

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