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⑤④ **Copper colloid and method of activating insulating surfaces for subsequent electroplating.**

⑤⑦ The invention relates to colloidal copper solutions containing palladium useful for activating non-conductive substrates for subsequent electroless and electrolytic plating.

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COPPER COLLOID AND METHOD OF ACTIVATING INSULATING
SURFACES FOR SUBSEQUENT ELECTROPLATING

Technical Field

5 The invention relates to colloidal copper solutions containing palladium useful for activating non-conductive substrates for subsequent electroless and electrolytic plating.

10 Background of The Invention

 Numerous applications are found commercially today where it is desirable to have a plastic, glass, or other like non-conductive substrate provided with a metal coating on its surface either as a continuous coating or
15 as a patterned or discontinuous coating. Among the applications for such metal coated articles of normally non-conductive materials are circuit boards, automobile hardware, various building and construction hardware, toys, buttons, and the like.

20 In all such applications the process requires the activation of the non-conductive substrate since electroplating cannot be carried out on such a substrate and electroless plating will also not deposit on such non-conductive surfaces. The activation is followed by an
25 electroless plating which will carry a current for subsequent electroplating or which can alternatively be further electrolessly plated with the same or a different metal.

30 Commercial prior art activating systems have generally relied upon one or more of the noble metals, such as palladium. A process that has been employed commercially, involves a colloidal dispersion of palladium and tin chloride salts as disclosed in U.S. Patent No. 3,011,920 to Shipley.

Before activation of the non-conductive substrate, it is generally subjected to various cleaning and etching steps known in the art.

5 The U.S. Patent No. 3,011,920 to Shipley,
referred to above, discloses the use of colloidal disper-
sions of various metals in combination with reducing
agents to achieve activation of non-conductive substrates
for subsequent electroless plating. The working examples
utilize noble metals or hydrous oxides thereof as the
10 colloidal particles and stannous chloride or tannic acid
as a reducing agent. The specification in column 2 refers
to the fact that other metals, including numerous non-
noble metals such as copper, may similarly be employed to
catalyze non-conductive substrates for electroless
15 deposition.

The U.S. Patent No. 3,657,002 to Kenney discloses
a process for preparing hydrous oxide colloids of many
different metals including both noble and non-noble metals
for treating or coating non-conducting substrates for
20 subsequent electroless plating.

U.S. Patent No. 3,993,799 issued to Feldstein
also discloses the use of a non-noble metal hydrous oxide
colloid for treating non-conductive substrates followed by
reduction of the hydrous oxide coating on the substrate to
25 achieve at least a degree of activation for subsequent
electroless plating.

U.S. Patent No. 4,239,538 to Feldstein discloses
solutions containing copper ions, stannous ions and a
phenol or creosol as a so-called linking agent for
30 treatment of non-conductive substrates for subsequent
electroless plating, while Feldstein's U.S. Patent No.
4,259,376 discloses an emulsion containing copper as the
principal catalytic agent and a catalytic promoter
consisting of a number of non-noble metals to yield an

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enhanced catalytic activity for electroless plating of non-conductive substrates.

U.S. Patent No. 3,958,048 to Donovan discloses a process for the surface activation of non-conductive
5 substrates for electroless plating by treating the surface of the substrate with an aqueous composition containing catalytically active water insoluble particles formed by a reaction of a non-noble metal and a water soluble hydride in the presence of a water soluble organic suspending
10 agent. Copper salts are disclosed as one of the non-noble metals, dimethylamine borane (DMAB) as one of the hydrides, and gelatin as one of the possible organic suspending agents.

The use of copper colloids for the activation of
15 non-conductive substrates in place of the palladium colloids has recently become commercial to a limited extent. With the use of copper activating colloids it has generally been necessary to utilize a fast electroless copper bath in order to obtain good coverage of the
20 non-conductive substrate by the electroless plating step. When the copper activating colloids are utilized and a slow copper electroless bath employed, the degree of coverage of copper by the electroless bath is decreased significantly. For example, when some copper colloids are
25 utilized with a fast bath, 100% coverage can be obtained, but when a slow electroless bath is used the coverage obtained may only be on the order of 25 to 35 percent of the surface of the non-conductive substrate. Thus, one could say that the catalytic activity of a copper colloid
30 may be sufficient when employing a fast copper electroless bath, but insufficient when a slow electroless copper bath is employed. These electroless copper baths, fast and slow, are well known within the industry, and can be characterized both by the deposition speed of the baths
35 and their stability. Generally, however, a fast

electroless copper bath would be capable of depositing about 100 micro inches of copper onto a conductive or activated surface in about 30 minutes, while a slow electroless copper bath would be capable of depositing 35 to 40 micro inches of copper within about 30 minutes. Fast electroless copper baths are less stable and can only be utilized for short periods of time if not properly replenished and controlled. This instability is generally due to a rapid imbalance and/or depletion of the chemical makeup of the baths during operation. Thus, these fast baths must be frequently analyzed and adjusted to the desired chemical balance in order to obtain electrolessly plated substrates suitable for subsequent electroplating and commercial use. This is a cause of great concern in commercial production of such items as circuit boards. A slow copper electroless bath, however, is quite stable and can be used for long periods of time without chemical adjustments, and the use of such bath is highly desired by industry, particularly where only a flash electroless copper coating is desired or a deposit in the range of 35 to 40 micro inches in thickness. This thickness is often desired in the production of circuit boards.

There are many variables which determine whether an electroless copper bath is fast or slow. One of the more important factors in determining the speed of such baths is the temperature used during the electroless plating operation and, to a lesser extent, the amount of chemicals utilized to make up such baths. For example, a fast bath can constitute an aqueous solution containing 8 ml/l of a 37% formaldehyde solution, 10 g/l of sodium hydroxide, and 3 g/l of copper metal supplied by a suitable salt, such as copper sulfate. When operating this bath at about 120°F, it is considered to be a fast bath and will deposit about 100 micro inches of copper onto a conductive or properly activated surface in about

30 minutes. An example of a slow bath would be an aqueous solution containing about 20 ml/l of a 37% formaldehyde solution, 15 g/l of sodium hydroxide, and 3 g/l of copper metal; again supplied to the solution by means of a
5 suitable salt. When this bath is operated at about 75°F or room temperature, it is considered to be a slow bath and it will deposit between about 35 and 40 micro inches of copper to a conductive or activated surface in about 30 minutes. When such a slow bath is operated at higher
10 temperatures, such as about 95°F, it becomes a fast electroless copper bath. All of this is known in the art and the terms "slow" and "fast" electroless copper baths are terms of the art.

All of these electroless copper baths also
15 contain stabilizers and complexing agents for the copper. These stabilizing and complexing agents are also well known in the art. The applicant prefers to use divalent sulfur compounds as stabilizing agents, such as those disclosed in the Schenble U.S. Patent No. 3,361,580, plus
20 a small amount of cyanide ion. The amount and type of stabilizing agent can be varied in these baths depending upon whether the bath to be employed is a slow or fast bath. Generally it is advisable to increase the amount of stabilizing agent when a fast bath is being employed.
25 This is also well known to those skilled in the art and regulation of the stabilizing agent to obtain optimum stability will depend upon the makeup of the particular bath being employed and the operating temperature of the bath.

30 The complexing agents are also well known in the art and include such materials as the carboxylic acid type complexing agents, amine carboxylic acid complexing agents, such as EDTA, aliphatic carboxylic acids, such as citric acid, tartarates, and Rochelle salt.

Disclosure of The Invention

This invention comprises the discovery that the addition of a small amount of ionic palladium (reducible to palladium metal) to copper colloid activating solutions significantly increases the activation of the non-conductive surface and therefore the coverage of the electroless copper deposition when utilizing a slow electroless copper bath. For example, the coverage obtained by utilization of a slow electroless copper bath with a palladiumless copper colloid can be increased from between 25 and 35 percent coverage to 75 percent and above coverage. The extent of the increase in coverage or catalytic activity will depend upon the particular copper colloid being employed, but in all cases tested by the applicant, the increase in coverage has been found to be very significant.

It is advantageous to add as little palladium metal as possible to the copper colloids for economic reasons. A sufficient amount of palladium metal should be added to increase the coverage of the electroless copper deposit to that desired. The most advantageous amount of palladium metal has been determined to date to be about 20 parts per million (ppm) although considerably lower amounts can be used. The minimum amount of palladium metal will also depend somewhat upon the speed of the electroless copper bath and the particular ionizable palladium compound employed.

Although the applicant has given an example of a slow bath, which will deposit approximately 35 to 40 micro inches of copper in about 30 minutes, slightly faster baths could be employed if the coverage is not sufficient. For example, if one obtains a coverage of 90% with such an electroless copper bath, and desires higher coverage for subsequent electro-deposition, one can increase the speed of the bath by appropriate chemical

adjustment or increase in the temperature to obtain the desired coverage so long as the speed of the bath is not increased to a degree that the bath becomes fast or unstable. For example, the electroless copper bath could
5 be regulated to give a deposit of 50 to 60 micro inches to improve coverage while still maintaining the stability of the bath. Increase in the coverage may also be accomplished by regulation of the palladium content.

The upper limit of palladium metal will depend
10 upon the particular ionizable palladium compound added to the bath, the effect of the anion of the ionizable palladium metal on the stability of the bath, and the stability of the bath itself. Thus, one can add the palladium metal in an amount which will still retain the
15 stability of the colloid. When utilizing a fairly stable colloid to begin with, the addition of palladium metal as palladium tetra-ammonium chloride in excess of about 80 ppm of palladium metal has been found to cause coagulation of the colloid and rendering it unstable. With colloids
20 which are less stable to begin with, the colloids may coagulate or be rendered unstable when amounts of palladium metal are added thereto of less than about 80 ppm. Thus, the maximum amount of palladium metal that is added is that which will retain sufficient stability of
25 the colloid so that the non-conductive substrate can be adequately activated by the colloid for subsequent electroless plating.

The palladium is added to the colloid in the ionic state. Experiments to date have shown that most any
30 palladium compounds or salts capable of ionization and reduction can be used, such as the palladium chloride acid salt and palladium tetra-ammonium chloride; the latter being presently preferred. The addition of palladium metal, from commercial colloidal palladium activating
35 catalysts in the amount of 20 ppm of the palladium metal,

causes precipitation or coagulation of the copper colloid, and when an attempt is made to use this copper colloid containing the palladium metal added from a palladium activating colloid, zero coverage is obtained when
5 utilizing a slow electroless copper bath. When utilizing a palladium metal colloid containing 20 ppm of palladium alone without the presence of the copper colloid, only 60% coverage is obtained from the slow electroless copper baths.

10 The ionic palladium added to the copper colloid is reduced at some stage to palladium metal prior to electroless plating. Thus, the palladium compounds can be added directly to the copper colloid if it contains an excess of reducing agent or during the preparation of the
15 colloid if the colloid is prepared by a reduction technique, such as disclosed in the above U.S. patent to Donovan. The palladium can also be added to colloids prepared by a precipitation process, such as disclosed in the Feldstein Patent No. 3,993,799 and the ionic palladium
20 reduced after the colloid has been coated on the non-conductive substrate by immersion of the coated substrate into a reducing agent.

In all of the following examples, the test panels were composed of the standard glass-epoxy material
25 normally used in the production of printed circuits and containing no copper cladding. The electroless copper bath utilized was a slow copper bath containing 20 ml/l of 37% formaldehyde, 15 g/l of sodium hydroxide, 3 g/l of copper metal as copper sulfate, a divalent sulfur
30 stabilizer, such as disclosed in U.S. Patent 3,361,580, in a sufficient amount to stabilize the bath, an amine carboxylic acid complexing agent for the copper and a small amount of cyanide ion. The bath was operated at 75°F. The palladium metal was added as palladium
35 tetra-ammonium chloride. The time of immersion in the

electroless copper bath was approximately 30 minutes.

Example 1

A copper colloid was prepared in accordance with Example 2 of the Donovan Patent No. 3,958,048, and a glass filled epoxy panel was immersed in the colloid, and an attempt was made to electrolessly plate the treated panel with the above-noted slow electroless copper bath. No coverage or plating of copper was noted after 30 minutes immersion time. 20 ppm of palladium metal was then added to this same colloid as palladium tetra-ammonium chloride. The palladium ammonium chloride was added to the colloid after its preparation since the prepared colloid contained sufficient excess reducing agent capable of reducing the ionic palladium contained therein to palladium metal. The panel was activated by the copper colloid containing the palladium by immersion, and then electrolessly plated with the same copper bath. The coverage of the electroless deposit on the panel was found to be about 70% after 30 minutes.

Example 2

An hydrous oxide colloid was prepared according to Example 12 of the Feldstein Patent 3,993,799 by the precipitation method utilizing copper acetate and ammonium hydroxide. This hydrous oxide colloid was then used to coat the glass epoxy panel and the hydrous oxide reduced by immersing the treated panel into a potassium borohydride solution. The panel was then subjected to electroless deposition by means of the slow electroless copper bath described above. The coverage obtained from the electroless copper bath was approximately 25%.

20 ppm of palladium ammonium chloride was added to the same hydrous oxide colloid described above prior to reduction of the coated panel and a panel coated therewith. After reduction in the same potassium borohydride solution, and electroless plating with the

same electroless copper solution, an 80% coverage of the panel was obtained.

Example 3

5 A copper colloid was prepared in accordance with Example 4 of the Feldstein Patent No. 4,259,376 without the manganese chloride. The standard glass epoxy panel was treated with this colloid and subjected to the standard electroless solution as described above. The coverage of the electroless copper was found to be about 20%.

10 Example 4 of Feldstein was again repeated adding the manganese chloride and the coverage of the electroless copper deposition was found to be about 35%. When the same colloid was produced and 20 ppm of palladium tetra-ammonium chloride added thereto in place of the manganese chloride, and the procedure repeated, the coverage from the standard slow electroless copper bath was found to be approximately 75%.

20 The types of non-conductive substrates that can be activated according to this invention are the same as those disclosed in the patents referred to above. The colloids of the invention are particularly advantageous for activating plastics such as epoxy-glass, phenolic glass, ABS-glass, phenolic-paper, etc., and the non-conductive portions of laminated circuit boards. These circuit boards, as is well known, are generally composed of such plastic compositions having two thin sheets of copper foil laminated to both sides of the plastic and having appropriate holes drilled through both copper sheets and the plastic. The plastic portions of the laminate, such as that exposed by the drilled holes, must be electroplated to provide continuity of electric conductivity throughout the circuit board. Thus, the exposed plastic portion of the laminate must be activated

for electroless metal plating and subsequent electro metal plating.

To activate such circuit boards, it is advantageous to use colloids which have a particle size of between about 10 and 100 millimicrons, a particle zeta potential of between about +3 and +13 millivolts (MV), advantageously between about 4 and 10 MV, and which colloid contains a sufficient number of particles to sufficiently activate the surface of the non-conductor so it can be successfully electrolessly plated.

Actually the colloidal copper particles themselves do not have a zeta potential of between about +3 and +13 MV. The particles are altered by treatment with the suspending or stabilizing agent to possess the desired zeta potential. Thus, the suspending agent itself has a zeta potential of a sufficient value to form a composite particle which has the desired zeta potential or somehow alters the zeta potential of metallic copper and/or copper oxide particles to within the desired range. Thus, a stabilizing agent may have a zeta potential of about +18 MV when combined with copper particles having a minus zeta potential causing the composite particles so formed to have a zeta potential within the desired range of +3 to +13 MV. It would be routine for a person skilled in the art to measure zeta potentials and select the correct suspending agent to produce a colloid having the desired zeta potential. Not all suspending agents will give the desired zeta potential; it depends on the purity of the suspending agent and/or the manner in which it was produced or purified, the presence or absence of ions, etc. An example of such a suspending agent is acid washed Type A gelatin. It should also be a relative pure Type A gelatin, free of significant impurities, such as excess sodium ions, that would interfere with obtaining the

desired zeta potential. Other suspending agents could be used in place of gelatin, so long as they possess the desired zeta potential and do not highly disassociate and migrate from the copper particles.

5 The invention does not exclude reduction of the
ionizable palladium compound in a solution separate from
the copper colloid in the presence of a suitable suspend-
ing agent such as gelatin and adding the palladium metal
in this form during or after the preparation of the copper
10 colloid even though such a process is somewhat more
complicated.

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Claims:

1. The method of preparing a copper colloid for activation of a non-conducting substrate which comprises adding a minor amount of an ionizable palladium compound to the copper colloid and reducing the palladium compound therein to form metallic palladium particles in an amount sufficient to maintain the copper colloidal particles as the primary activating agent.

2. The method of claim 1 in which the copper colloid contains excess reducing agent after its preparation and the palladium compound is added thereto after the copper colloid has been prepared.

3. The method of activating a non-conducting substrate comprising treating the substrate with a composition containing a minor amount of an ionizable palladium compound and a major amount of hydrous oxide copper colloid particles containing an insufficient amount of reducing agent to reduce the ionizable palladium compound to palladium metal and reducing the hydrous oxide colloid and the ionizable palladium compound to metallic copper and metallic palladium while adhered to said conducting substrate and in which the metallic copper is the primary activating agent.

4. An aqueous copper colloid for the activation of non-conductive substrates for subsequent electroless plating comprising colloidal particles of metallic copper and a minor amount of palladium metallic particles formed by reduction of an ionizable palladium compound within said copper colloid after or during preparation of the copper colloid by reduction of a copper compound.

5. The colloid of claim 4 in which the palladium are reduced to metallic form from palladium and copper and copper compounds in the presence of a suspending agent such as gelatin.

6. The colloid according to claim 5 in which the palladium compound is separately reduced to metallic palladium in the presence of a suspending agent such as gelatin and is subsequently added to the copper colloid during or after preparation of the copper colloid.

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7. A non-conductive substrate having activating sites thereon sufficient to permit electroless plating thereon in which the activated sites comprise a mixture of a major amount of copper metal and a minor amount of palladium metal.

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8. A stable aqueous colloid for the activation of non-conductive substrates for electroless plating which comprises particles of metallic copper and/or copper oxide having a particle size of between about 10 and 100 millimicrons and having a zeta potential between about +3 and +13 millivolts, said colloid having an amount of particles to activate the surface of a non-conductor and containing a minor proportion of palladium produced by reduction and from an ionizable palladium compound within said colloid or during preparation of the colloid by reduction of a copper compound or by a separate reduction of the palladium in the presence of a colloid such as gelatin.

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EINSCHLÄGIGE DOKUMENTE			KLASSIFIKATION DER ANMELDUNG (Int. Cl. ³)
Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich, der maßgeblichen Teile	betrifft Anspruch	
D,Y	US - A - 3 011 920 (C.R. SHIPLEY) * Examples 1-7; claims * --	1-8	C 23 C 17/00// C 25 D 5/54
Y	US - A - 4 008 343 (R.L. COHEN et al.) * Claims * --	1-8	
Y	US - A - 4 042 730 (R.L. COHEN et al.) * Columns 2-4; claims * --	1-8	
X	US - A - 4 048 354 (N. FELDSTEIN) * Examples, especially example 1; claims * --	1-8	C 23 C C 25 D
Y	US - A - 4 131 699 (N. FELDSTEIN) * Examples; claims * --	1-8	
Y	US - A - 4 153 746 (H.D. KILTHAU) * Example; claims * --	1-8	
Y	US - A - 4 180 600 (N. FELDSTEIN) * Examples; claims * --	1-8	
Y	US - A - 4 273 804 (N. FELDSTEIN) (16-06-1981) * Examples; claims * --	1-8	
Y	US - A - 4 293 591 (N. FELDSTEIN) (06-10-1981) * Examples; claims * ----	1-8	
Der vorliegende Recherchenbericht wurde für alle Patentansprüche erstellt.			
X			
Recherchenort			Abschlußdatum der Recherche
WIEN			11-06-1982
			Prüfer
			SLAMA