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⑦ Applicant: **LEA-RONAL, INC., 272 Buffalo Avenue,**
Freeport, N.Y. 11520 (US)

⑦② Inventor: **Brasch, William Robert, 11 Canterbury Lane,**
Nesconset N.Y. 11767 (US)

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⑦④ Representative: **Hansen, Bernd, Dr.rer.nat. et al,**
Hoffmann . Eitle & Partner Patentanwälte
Arabellastrasse 4, D-8000 München 81 (DE)

⑤④ **A stable aqueous colloid for the activation of non-conductive substrates and the method of activating.**

⑤⑦ A stable colloidal solution useful for activating non-conductive substrates for subsequent electroless plating containing colloidal copper and/or copper oxide particles as the effective activating agent, said particles having a zeta potential between about +3 and +13 millivolts a particle size between about 10 and 100 millimicrons and being stable and capable of activating a non-conductive substrate over practically the entire pH range and advantageously between a pH of about 2 through 8. Also a method of activating a non-conductive substrate using the stable colloidal solution is disclosed.

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A stable aqueous colloid for the activation of non-conductive substrates and the method of activating

This invention relates to a stable aqueous colloid for the activation of non-conductive substrates and the method of activating. Namely the invention relates to a novel copper colloid for the activation of non-conductive materials, particularly plastics, to prepare such materials for subsequent metal coating by conventional electroless and electroplating.

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 plating on its surface either as a continuous coat or as a patterned or discontinuous plating. Among the applications for such metal plated articles are included automobile hardware, various building and construction hardware, toys, buttons, circuit boards and the like where the coating is generally, though not always, substantially continuous over one surface or more.

In all such applications the process requires the activating of the non-conductive substrate since electroless or electroplating cannot be carried out on such a substrate. The activating is followed by an electroless plating which will carry a current for subsequent electroplating.

Commercial prior art activating systems generally rely upon one or more of the noble metals and most particularly palladium. For example, one of the earliest methods of activating such substrates involved a two-step operation involving first immersion of the substrate in a stannous chloride solution followed by a second immersion in an acid palladium chloride solution. Subsequently a one-step process has been employed commercially, involving



a colloidal dispersion of palladium and tin chloride salts as disclosed in U.S. Patents Nos. 3,011,920 and 3,672,923.

The noble metal of the activating solution, such as palladium, serves to activate, catalyze, or seed the non-conductive substrate for the subsequent electroless plating bath. After a few minutes in the electroless metal plating bath, the article will have a very thin coating of the selected metal of the bath thereon. It is then rinsed and the article may then be further plated with the same or another metal by well known electroplating processes.

The U.S. Patent No. 3,011,920 to Shipley, referred to above, discloses the use of colloidal dispersions of various metals in combination with reducing agents to achieve activation of insulative substrates for subsequent electroless plating. The working examples utilize noble metals or hydrous oxides thereof as the 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, may similarly be employed to catalyze non-conductive substrates for electroless deposition.

The U.S. Patents Nos. 3,657,002, 3,783,005 and 3,950,570 to Kenney disclose processes for preparing hydrous oxide colloids of many different metals including both noble and non-noble metals for treating or coating non-conducting substrates for subsequent electroless plating.

U.S. Patents Nos. 3,993,799 and 4,136,216 issued to Feldstein also disclose the use of non-noble hydrous oxide or metallic colloids for treating non-conductive plastics followed by reduction of the hydrous oxide coating on the plastic to achieve at least a degree of activation for subsequent electroless plating.

U.S. Patent No. 3,958,048 to Donovan discloses a process for the surface activation of non-conductive 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 agent. In order to be operable, the suspension is required to have a pH below 5 or from 7.7 to 9.5. 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 many possible organic suspending agents. In addition to the inherent disadvantage of having to maintain the composition of Donovan within the specific pH ranges disclosed in order to maintain the compositions in a catalytically active state, the compositions made in accordance with the Donovan disclosure are not sufficiently stable for practicable or commercial use. It has been found, for instance, that the compositions of the examples break down during a period varying from a few hours to a few days rendering the suspensions commercially impractical.

Disclosure of The Invention

This invention relates to a novel stable copper colloid having a particle size between about 10 and 100 millimicrons (mm), a particle zeta potential between about +3 and +13 millivolts (mv) and containing a sufficient number of particles to activate a non-conductive substrate that it can accept an electroless deposition. The colloids of this invention are also stable and capable of activating a non-conductive substrate over practically the entire pH range, and advantageously between a pH of about 2 through 8. The ability to use these colloids over a wide pH range lends more versatility to the colloids

and permits continued operation under commercial conditions where pH changes occur during operation.

Detailed Description

5 The colloids of this invention can be made by using a stabilizer or suspending agent which will produce or impart to the metallic and/or oxide copper particles of the colloid a zeta potential of between about +3 and +13 mv, advantageously between about +4 and +10 mv. The
10 suspending agent should have a zeta potential which, when combined with the colloidal copper particles, will produce particles having a zeta potential between about +3 and +13 mv. If the copper particles have a negative zeta
15 potential, it may be necessary to use a suspending agent having a high positive zeta potential such as +18 mv to impart the desired zeta potential to the particles of the colloids.

 The use of certain types of gelatin are examples
20 of suspending agents that can be used to produce colloids having the desired zeta potential. Typically an acid washed Type A gelatin of sufficient purity can be used.

 Thus, the type of gelatin, the manner in which it was produced or purified, and its purity also play a
25 role in the ability of the gelatin to impart the desired zeta potential to the colloidal copper particles. The suspending agent or gelatin should be sufficiently free of interfering ions, such as excess sodium ions, which will interfere with imparting the desired zeta potential
30 to the particles of the colloid. Other suspending agents could be used in place of gelatin so long as they possess the desired zeta potential, or are capable of imparting to the particles of the colloid a zeta potential between about +3 and +13 mv, and do not highly disassociate and
35 migrate from the copper particles. A person skilled in the art can measure zeta potentials and select the correct

suspending agent to produce a colloid with particles having the desired zeta potential when given the teachings of this application.

As can be observed from the prior art, non-noble
5 colloids can be prepared in many ways, but they all suffer various deficiencies which prohibits their commercial use. For practical commercial use the colloids, particularly on copper clad circuit boards, must have the properties of stability, particle size and zeta potential. Colloidal
10 particles must deposit on a non-conductive surface in a sufficient amount and of sufficient uniformity so that subsequent electroless plating will produce a deposit of sufficient uniformity to permit subsequent electroplating. The colloidal particles must also adhere to the surface
15 to prevent peel-off after electroless and electroplating during fabrication and use of the end product. In other words the colloid cannot spot deposit on the substrate. Non-uniform or spotty deposits can be caused by different factors, such as an insufficient number of particles in
20 the colloid, a colloid which is too stable, agglomerated colloidal particles, due to the instability of the colloid, too many of the particles are too small, etc. For example, a colloid having particles of a zeta potential of less than about +2 mv are not stable and do not adequately
25 adhere to or activate non-conductive surfaces, such as glass.

The particles of applicant's colloids not only have a low positive zeta potential but a small particle size which renders them uniquely suitable for activating
30 plastics and the plastic portions of circuit boards, particularly where the plastic contains a glass filler.

The prior art believed to be the closest and known to the applicant is the Donovan patent No. 3,958,048. Although Donovan does mention gelatin, there is no recog-
35 nition of its significance in producing stable colloids

which can be used to activate a non-conductive substrate at a pH above 5 and below 7.7. In fact, Donovan teaches the colloids made according to his invention are inoperable within the pH range. Further, the broad term "gelatin" does not disclose or teach applicant's specific stabilizers having a specific zeta potential capable of imparting the desired zeta potential to the particles of the colloid.

As a comparison, the applicant repeated Examples 1 and 2 of the Donovan patent 3,958,048 and varied the pH. With respect to Example 1, the particles had a zeta potential of about -20 at a pH of 6, but the velocity of the particles varied during the test, that is, some particles were much slower than the average. At a pH of 4, the particles had a zeta potential of about -25.

With respect to Example 2, at a pH of 2 the particles had a zeta potential of about +1, and at a pH of 4 a zeta potential of about -1. At a pH of 6, the zeta potential was about -2.

However, when a relatively pure acid washed Type A gelatin was substituted for the Daxad 11, the colloid had a zeta potential of about +9 mv at a pH of 4, and a zeta potential of +13 mv at a pH of 2. With respect to Example 2, substituting the same gelatin for the Daxad 11, the particles had a zeta potential of about +3 mv at a pH of 6 and a zeta potential of +4 mv at a pH of 2. At a pH of 5 the particles had a zeta potential of +7 mv and when dextrin was eliminated and only the gelatin used, the particles had a zeta potential of +13 mv.

The copper colloids are unique and novel and are particularly advantageous for the activation of copper clad circuit boards employing glass filled plastics. In such cases there are at least three different materials to be dealt with, namely the copper clad, the plastic, and the glass filler. The activating colloid must adequately adhere to all three of these materials or the

-7-

subsequent electroless and electroplate will peel off during subsequent fabrication or use. With regard to the copper portion, it is advisable to remove excess colloid particles using an aqueous stripping solution, such as neutral hydrazine hydrate. The activation of such circuit boards can be accomplished by using applicant's novel colloids which have a particle size of between about 10 and 100 millimicrons and a particle zeta potential of between about +3 and +13, preferably between about 4 and 10. Part of the novelty of colloids of this invention resides in the fact that the particles are not only small but also have a low positive zeta potential. The colloids are also stable, that is, the particle size does not appear to grow causing the particle to precipitate out leaving a few particles to effect activation or to cause alteration of the zeta potential to a degree that the particles will not adhere sufficiently to the substrate. This stability of applicant's colloid is advantageously maintained over a wide pH range. Stability over a narrow pH range would not be practicable in commercial production since the pH would necessarily be altered during operation.

Claims:

1. A stable aqueous colloid for the activation
5 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
10 of particles to activate the surface of a non-conductor.

2. A colloid according to claim 1 in which
the colloid has a pH of about 7.

15 3. A colloid according to claim 1 in which
the colloid has a pH between about 4 and 8.

4. A colloid according to claim 1 in which
the colloid has a pH between about 2 and 8.
20

5. The method of activating a non-conductive
substrate for electroless metal deposition by means of
a colloid containing metallic copper and/or copper oxide
particles characterized in treating the metallic or oxide
25 particles with a suspending agent having a sufficient
zeta potential to impart to the metallic or copper oxide
particles a zeta potential between about +3 and +13 milli-
volts.

30 6. The method of claim 1 in which the copper
and/or copper oxide particles after treatment with the
suspending agent have a particle size between about 10
and 100 millimicrons.

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European Patent
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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<u>AU - B - 422 372</u> (PHOTOCIRCUITS CORPORATION) + Pages 13-15; claims + --	1	C 23 C 17/00 C 23 C 3/00 C 25 D 5/00
	<u>US - A - 4 020 197</u> (H.STEFFEN) + Claims + ----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
			C 23 C C 25 D
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
X	The present search report has been drawn up for all claims		
Place of search VIENNA		Date of completion of the search 09-03-1981	Examiner SLAMA