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ELECTROLESS PLATING COMPOSITION

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ABSTRACT OF THE DISCLOSURE

A method of preparing a non-conducting plastic base for electroless plating of metal thereon by treatment with a dilute solution of a stannous compound in a glycol ether.

The present invention is directed to plating of metals, such as copper and nickel, on non-conducting bases, and more particularly to electroless deposition of the metal.

Procedures of this kind have been in use for a considerable time. They treated the plastic base to clean the surface, then sensitized the base which was then treated with a palladium chloride solution which was a catalyst or activator, after which the copper salt solution was applied to form the plating.

Two techniques for preparing the surface of plastic prior to electroless copper deposition had been developed employing either etching or conditioning solutions in a special bath. Both etching and conditioning solutions are highly acidic solutions that chemically alter the surface of the plastic without overly marring or breaking down its molecular structure. Unlike etching, conditioning does not roughen the surface. One process employs an acid dip conditioner followed by sensitizing and activating solutions which prepare the surface for an electroless copper deposit.

The sensitizer normally used is an acidified solution of stannous chloride. The other process uses an intermediate step following the etching treatment. This step forms a thin, water-soluble film of resin on the surface of the plastic. This resin is not crosslinked at this point, so as to allow the absorption of a sensitizing metal from solution in a later step. Following this step, the resin film is crosslinked and the surface prepared catalytically for the deposition of electroless copper in a pre-plate solution.

Such processes required a series of steps of treatment of the surface of the base with intermediate revising after each step. This introduced the necessity for a substantial amount of equipment and considerable amount of labor for the operations. One of the prior processes involved the application of a chromate chemical etchant, which had a number of disadvantages in that considerable time was necessary for the treatment, the chemicals were corrosive and poisonous creating a hazard for the workmen, and elevated temperatures were necessary in carrying out the treatment, as well as disposal problems of spent solutions.

The present invention is intended and adapted to eliminate the difficulties and disadvantages inherent in prior processes and to provide a one-step process thereby eliminating the necessity of a three-step process (pre-cleaning, etching and sensitizing), as heretofore described, for the preparation and conditioning of substrate prior to the deposition of electroless plating.

The invention is based on the discovery that a glycol ether solvent has all the properties necessary to properly prepare the surface of a plastic body so as to hold the copper plate firmly in position. Most solvents leave the surface of a plastic, such as an acrylic resin, hydrophobic or do not attack the surface at all or do not wet the surface. On the other hand glycol ethers such as the alkyl

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ethers of ethylene or propylene glycols and the dialkyl ethers of such glycols attack the surface of an acrylic resin, and are sufficiently soluble in water so that they rinse off the work readily. As such these solvents are readily removable and are not adsorbed onto the resin. In addition, they have a mild etching action on the base.

When such glycol ethers are used alone to condition the surface it is found that the eventual plate is apt not to be even and it is sometimes difficult to control the action thereof on the base. It has been found that stannous chloride is soluble in these glycol ethers and also that such a solution when applied to the base conditions the surface, sensitizes it and cleans off any film of oil or other substances on the surface due to handling. The effect of the solution is definite and readily controllable. Therefore, such a solution is preferred for the operation.

By the use of stannous chloride dissolved in a glycol ether, soluble or partially soluble in water, the three steps previously employed are combined into one step. The use of this one step method increases the adhesion properties on the surface of the plastic making the metal-to-plastic bond stronger and more readily acceptable to subsequent deposits of electroless copper. By the use of this disclosure the plastic is cleaned, etched and swollen to expose the pores, made hydrophilic, and sensitized in one bath. On subsequent rinsing and the rise in pH, the stannous chloride is precipitated as the oxide or hydroxide, and excess solvent is readily leached from the plastic, reducing the swelling and firmly bonding the sensitizer to the plastic mechanically as well as the chemical bonds which are present.

The glycol ethers used may be of the ethylene glycol ether ("Cellosolve") or diethylene glycol ether ("Carbitol") family, methyl to the butyl or amyl ethers being most readily available. Other glycol ethers such as propylene glycol ethers may also be used. The said glycol ethers are those in which the alkyl radicals have from 1 to 5 carbon atoms. The stannous chloride content may be as low as .1% up to the saturation point, although above 5% the bulk of the stannous chloride is rinsed from the work. Other sensitizers such as titanous chloride may be treated in a like manner.

The time of treatment with the stannous chloride-glycol solution may vary considerably. A treatment for about one minute will result in a bright copper deposit because of the extreme thinness of the deposit, since it has a smoother surface. Such deposits are useful primarily for decorative articles not subject to wear or abrasion. The treatment may be as long as ten or more minutes of etching time resulting in good adhesion of the plating on the plastic base, making an article which is quite resistant to abrasion. It has been found that etching for about 5 to 8 minutes gives highly satisfactory results. The operation is conducted at approximately room temperature.

The following specific example is given as a suitable bath for acrylonitrile-butadiene-styrene plastic (A.B.S.):

Composition—	Percent by weight
"Cellosolve" (ethylene glycol ether)	99
Stannous chloride 2H ₂ O	1

Various other plastics may require an auxiliary solvent such as monohydric alcohols, esters of low carbon acids, ketones, halogenated hydrocarbons, such as chlorinated solvents, said compounds having 1 to 8 carbon atoms, and acid activators which are advantageous where titanium dioxide filler is present, to increase the etch or swell or plastic. Among such acids are the lower aliphatic acids, such as chloracetic, butyric and others, even inorganic acids.

The stannous chloride-glycol solution in hydrochloric acid is placed in contact with the acrylic base for say 5 minutes. Then the base is rinsed with water to remove the

acid, whereby the pH rises and the stannous chloride breaks down to stannous hydroxide or oxide, being held on the surface of the base. The water becomes cloudy during the operation. Then, as in the prior art a 1% solution in water of palladium chloride in hydrochloric acid is applied to the base; it reacts with the stannous compound and is transformed to a colloidal form of palladium which becomes firmly keyed to the etched irregularities of the base.

The excess of solution is thoroughly rinsed off. There is applied to the clean wet surface a solution of a copper salt such as copper sulfate, containing sodium hydroxide and Rochelle salts and formaldehyde, forming a smooth, non-porous, highly adherent deposit.

The essence of the invention lies in the preliminary treatment of the base, which may be other resins or plastic non-conducting materials than acrylic resins. This treatment is by a substantially water-free solution of the stannous chloride in the glycols described herein. It eliminates the necessity for such pretreatments of the base as degreasing, abrading, cleaning, etc. It combines three steps of the prior art into one step and avoids the necessity of heating in the operation.

While the invention has been described by an example in which a certain proportion of the stannous chloride was used in solution in the glycol ether, such proportions may be varied within the scope of the invention. The procedure subsequent to the sensitizing may be that known in the art which includes the activation of the surface of the base with salts of palladium, gold, platinum and others. The strengths of the acid palladium solutions may vary over a considerable range, as is known. The electroless copper solutions for plating the sensitized base are also well known and have been described in the literature. The present process is useful for many purposes, as in the making of printed circuits, the coating of such non-conductive bodies as car handles, boat lighting fixtures and lamps, and many other items.

What is claimed is:

1. A method of treating a substantially non-conducting plastic base for electroless plating of a metal thereon which comprises preparing a solution consisting essentially of a reducible stannous compound in a glycol ether

selected from the class consisting of the alkyl ethers of ethylene glycol, diethylene glycol, and propylene glycol wherein the alkyl radicals have from 1 to 5 carbon atoms, and contacting said base with said solution for a sufficient time to etch the surface of said base, and then washing said treated base to remove excess of said solution.

2. A method of treating in accordance with claim 1 in which said solution contains at least 0.1% of said stannous compound.

3. A method of treating in accordance with claim 1 in which said compound is stannous chloride.

4. A method of treating in accordance with claim 1 in which said solution contains at least 0.1% of said stannous compound and up to saturation.

5. A method of treating in accordance with claim 1 in which said solution contains from about 0.1% to 5.0% of said stannous compound.

6. A method of treating in accordance with claim 1 in which said contacting is conducted at approximately room temperatures.

7. A method of treating in accordance with claim 1 in which the time of contact is from about 1 to 10 minutes.

8. A method of treating in accordance with claim 1 in which the time of contact is from about 5 to 8 minutes.

9. A method of treating in accordance with claim 1 in which there is present in said solution hydrochloric acid.

10. A composition for treating a substantially non-conducting plastic base for electroless plating consisting essentially of a solution in a glycol ether selected from the class consisting of the alkyl ethers of ethylene glycol, diethylene glycol, and propylene glycol wherein the alkyl radicals have from 1 to 5 carbon atoms of about 0.1% to saturation of stannous chloride.

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