

[54] **ELECTROLESS PLATING SOLUTION AND PROCESS**

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[57]

## ABSTRACT

A process and solution for electroless plating of articles with a highly-stabilized electroless plating solution while maintaining high plating rates. An article having a catalytic noble metal on its surface is first electrolessly plated with a thin coating of metal plating, and is further electrolessly plated in a solution having an inhibitor concentration which prevents plating on an article having the catalytic noble metal on its surface but does not prevent plating on an article having the thin coating of plating metal.

**12 Claims, No Drawings**

## ELECTROLESS PLATING SOLUTION AND PROCESS

### BACKGROUND OF THE INVENTION

In the past several years, a very considerable demand has developed for metal plating on nonconductive articles. This has been particularly true with plastic articles. In the finished product, the desirable characteristics separately inherent in the two component materials are combined, therefore offering technical and esthetic advantages for their utilization in numerous applications. For example, the characteristics of low weight and easy forming which have contributed to the widespread use of plastics become more serviceable when combined with the mechanical properties and attractive decorative effect afforded by metallic coatings. These factors promise that utilization of these products will continue to expand into more and more fields.

Since plastics are electrically nonconductive, the production of metal-plated plastics preliminarily involves the chemical deposition or plating of a conductive metallic layer on the plastic surface, a process referred to as electroless plating. Thereupon, if required, additional thicknesses of metals from metal salt solutions can be electrolytically deposited on the electroless layer. Various plastics can be electroplated as described above, including, but not limited to, acrylonitrile-butadiene-styrene (ABS), epoxides, polypropylene, polystyrene, and polysulphones. On these plastic substrates, a metallic layer, typically copper or nickel, is electrolytically deposited. Additional metallic thickness, typically copper, nickel, or chromium, can then, if required, be electrolytically deposited on the electroless layer.

In preparing plastics for electroless plating, the plastic is subjected to a sequence of operations prior to electroless metal deposition. The plastic surface is conditioned, generally by chemical etching, to produce a micro-porosity. The conditioned plastic is then subjected to treatment by which it is activated for electroless deposition of metal. Although a one-stage treatment can be used, a two-stage treatment in which the plastic is successively "sensitized" and "activated" is most commonly employed. In general terms, the first step involves immersion in a solution of stannous chloride-hydrochloric acid to sensitize the plastic surface by adsorption of stannous ions. This is followed by immersion in a solution of a noble metal salt, e.g., palladium chloride, to activate the plastic by a reaction resulting in the reduction of the noble metal ions to the metal. The noble metal film on the plastic article then acts as a catalyst in the electroless metal bath into which the activated plastic article is passed. The above-described steps, with intermediate rinses and cleansing, are well known and widely practiced in the electroless copper and nickel plating art.

A variety of electroless copper and nickel formulations are also known to the art. For example, electroless copper formulations essentially consist of a soluble cupric salt, such as copper sulfate; a complexing agent for the cupric ion, such as Rochelle salt; an alkali hydroxide for adjustment of pH; a carbonate radical as a buffer; and a reducing agent for the cupric ion, such as formaldehyde. The mechanism by which objects having catalyzed surfaces, for example, plastic having catalytic palladium metal in its surface, as previously discussed, are copper-plated autocatalytically in such solutions

has been explained in the literature, for example, U.S. Pat. No. 2,874,072, issued Feb. 17, 1959.

Electroless plating solutions of the type described above are, however, subject to rapid decomposition. In part, this is due to the catalytic nature of the plating reaction. Many substances, including copper, steel, nickel, iron, palladium, gold, silver and even dust particles, are catalytic to these solutions. These particles grow in the body of the solution and, if sufficiently numerous, can initiate precipitation and decomposition.

Heretofore, for example, it has been necessary to use plastic-lined tanks for electroless plating baths since metallic tanks, such as stainless steel tanks, would be plated with attendant loss of valuable chemicals. Even in plastic-lined tanks, scratches in the lining result in initiation of decomposition because the scratches provide recesses within which hydrogen, produced during the plating reaction, is concentrated.

The need for stabilization of electroless plating baths to minimize decomposition has been recognized. To this end, inhibitors or so-called catalyst "poison," such as compounds having a carbonate radical, e.g., sodium carbonate, sodium bicarbonate, cupric carbonate, have been added to electroless plating solutions. However, since these compounds also retard the rate at which electroless plating occurs, there has been a practical limitation to utilization of such compounds in concentrations sufficient to provide long-term solution stability. For similar reasons, elevated bath temperatures, while known to have the advantage of increasing the rate of deposition, have not been generally used because such temperatures also promote decomposition.

There has existed, therefore, a need for a means by which electroless plating baths could be stabilized for long-term usage without adversely affecting plating rates. Such a means would decrease chemical and production costs and would result in greater operating efficiencies.

### STATEMENT OF THE INVENTION

The present invention enables use of a highly stable electroless plating bath without adverse effect upon plating rates. In terms of process, it includes in an electroless plating process the step of immersing an article having a catalytic noble metal on its surface in an electroless plating solution to initiate deposition of the plating metal on the article. The article is removed when a thin film of plating metal has been deposited on the surface of the article. The article is then immersed in an electroless plating bath which has a concentration of an inhibitor sufficient to prevent deposition of plating metal on an article having the catalytic noble metallic surface but does not prevent deposition of plating metal on an article having the thin film of plating metal.

For convenience, the bath in which the thin film of plating metal is deposited is referred to herein as the "strike" bath, whereas the bath in which additional plating metal is deposited is referred to as the "plating" bath.

It will be recognized that electroless deposition of plating metal occurs in both the strike bath and the plating bath. In the strike bath, deposition of plating metal is initiated by the catalytic noble metal on the nonconductive surface; in the plating bath, deposition

of plating metal is catalyzed by the thin film of plating metal deposited in the strike bath.

The concentration of inhibitor in the plating bath is such that, if the article having a catalytic noble metallic surface were passed directly into the plating bath without first passing through the strike bath, no plating metal would be deposited on the article. The concentration of inhibitor in the plating bath insures a highly stable bath since an inhibitor concentration sufficient to prevent plating on a catalyzed surface also acts to prevent decomposition due to the presence of other metallic contaminants.

The compositions used in the strike bath may be any of those conventionally employed for electroless deposition of plating metal on a nonconductive article. When the process of the invention is utilized for electroless copper plating, a conventional electroless copper plating solution at room temperature is used in the strike bath. Formulations of electroless copper plating baths include, for example, the following compounds in aqueous solution within the ranges set forth below:

| Ingredient          | Molar Concentration                    |
|---------------------|----------------------------------------|
| Soluble Cupric Salt | 0.02 - 0.15                            |
| Complexing Agent    | 0.03 - 0.75                            |
| Reducing Agent      | 0.05 - 1.50                            |
| pH Adjustor         | Sufficient to give<br>pH from 12 to 14 |

Since only a thin film of copper is deposited in the strike bath, its volume can be small so that the solution can be economically replenished or discarded as decomposition occurs. For this reason, the strike bath can be operated without any inhibitor or a small amount of inhibitor.

In electroless copper plating, it has been found that the most effective inhibitors are water-soluble cyanides. These include alkali metal cyanides such as potassium cyanide and sodium cyanide, complex metal cyanides, and water-soluble nitriles, which are organic compounds including a —CN group. Formulations of electroless copper plating baths within the scope of this invention include compounds within the ranges set forth below:

| Ingredient                        | Molar Concentration           |
|-----------------------------------|-------------------------------|
| Soluble Cupric Salt               | 0.02 - 0.15                   |
| Complexing Agent                  | 0.03 - 0.75                   |
| Reducing Agent                    | 0.05 - 1.50                   |
| Alkali Hydroxide<br>(to pH 12-14) | 0.10 - 2.0                    |
| Cyanide Inhibitor                 | 0.0015 - 0.24                 |
| Water                             | Sufficient to make<br>1 liter |

It will be recognized that the concentrations of complexing agent and reducing agent are related to the concentrations of cupric ion in solution, and that the upper limit of reducing agent is one of convenience and economy since even high concentrations would not adversely affect the performance of the solution.

By the process of the present invention, it also becomes possible to operate the plating bath at an elevated temperature without significant decomposition problems. In this manner, the advantages of high plating rates resulting from operation at elevated tempera-

tures are gained without attendant loss of valuable chemicals and production problems.

#### DETAILED DESCRIPTION OF THE INVENTION

For convenience, the detailed description of the process and solution of the present invention is made with reference to electroless copper plating of acrylonitrile-butadiene-styrene, referred to below as ABS plastic. The conditioning and activation of the plastic are described in general, as these steps are not, as such, a part of the invention.

A molded ABS plastic part is cleaned, pre-etched with an organic chemical solvent, if required, and then etched in an etching chemical bath such as a mixture of chromic and sulfuric acids. After cleaning of the etched article, including rinsing in an alkaline cleaner, the article is sensitized in a stannous chloride-hydrochloric acid bath and then activated in a bath of a noble salt, such as palladium chloride, to provide a catalytic noble metal on the surface of the plastic. Following rinsing to remove excess palladium from the surface of the article, it is passed into the strike bath which forms a part of the process according to the present invention.

The strike bath can be a conventional electroless copper plating solution having a formulation such as the following:

| Ingredient       | Concentration              |
|------------------|----------------------------|
| Rochelle Salt    | 34 grams/liter             |
| Caustic Soda     | 12 grams/liter             |
| Copper Sulphate  | 7 grams/liter              |
| Sodium Carbonate | 6 grams/liter              |
| Formaldehyde     | 25 ccs./liter              |
| Water            | Sufficient to make 1 liter |

The strike bath is typically maintained at room temperature. The plastic article with palladium metal on its surface is immersed in the strike bath for from about 30 seconds to about 3 minutes and then removed. This is a sufficient period of immersion to enable deposition of a thin copper film over the entire surface of the article. The strike bath, in addition to preparing the article for deposition in the electroless plating bath, also serves as a collector for the bulk of the contaminants which otherwise would pass directly into the plating bath.

Upon removal from the strike bath, the plastic article having a thin copper deposit is passed directly into the electroless copper plating bath. In order to increase the rate of plating as described above, this bath is maintained at an elevated constant temperature, preferably a temperature somewhere in the range from 90° to 140°F. An example of a formulation for the copper plating bath is as follows:

#### EXAMPLE 1

| Ingredient            | Molar Concentration           |
|-----------------------|-------------------------------|
| Copper Sulfate        | 0.036                         |
| Rochelle Salt         | 0.138                         |
| Sodium Bicarbonate    | 0.11                          |
| Formaldehyde          | 0.11                          |
| Free Sodium Hydroxide | 0.125                         |
| Potassium Cyanide     | 0.006                         |
| Water                 | Sufficient to<br>make 1 liter |

The free sodium hydroxide referred to above is that quantity which is in addition to the amount required to form the chelate and to convert the sodium bicarbonate in the solution to sodium carbonate.

The plastic article is retained in the electroless plating bath for a period of from 3 to 6 minutes. During this period of time, additional thicknesses of copper sufficient to permit subsequent electrolytic metallic plating are deposited. After removal from the electroless plating bath, the article is rinsed and soaked, and, if electrolytic plating is required, is passed to the electroplating process.

ABS molded articles have been conditioned and activated as described above and then passed into a room temperature copper strike bath having a formulation similar to the example given above. The articles having a thin copper surface deposit were then immersed in a plating bath having the composition of Example 1 above. The bath was maintained at a temperature of 105°F. The total time of immersion in the two baths was of the order of 4 to 5 minutes. The adherence of the electroless copper coatings thereby deposited was in excess of 20 pounds as measured by conventional pull test. The plating bath solution was maintained in operation without significant decomposition and with minimum replenishment of chemicals for a period of 2 to 3 months.

Since there is some tendency for the inhibitor to decrease the plating rate as it increases in concentration, it is preferable to maintain the inhibitor concentration at the level sufficient to suppress copper deposition on surfaces other than the thin copper coating of the plastic article. If, however, higher inhibitor concentrations are required to insure a stabilized solution, the rate of plating can be maintained substantially constant by increasing the cupric ion concentration together with the concentrations of the reducing agent and the caustic. The following examples of proportioned inhibitor-reducing agent-caustic in aqueous solutions will serve to further illustrate the practice of the process:

#### EXAMPLE 2

| Ingredient            | Molar Concentrations |
|-----------------------|----------------------|
| Copper Sulfate        | 0.02                 |
| Rochelle Salt         | 0.096                |
| Sodium Bicarbonate    | 0.11                 |
| Formaldehyde          | 0.067                |
| Potassium Cyanide     | 0.0016               |
| Free Sodium Hydroxide | 0.1                  |
| Temperature 100°F     |                      |

#### EXAMPLE 3

| Ingredient            | Molar Concentration |
|-----------------------|---------------------|
| Copper Sulfate        | 0.084               |
| Rochelle Salt         | 0.188               |
| Sodium Bicarbonate    | 0.11                |
| Formaldehyde          | 0.40                |
| Potassium Cyanide     | 0.10                |
| Free Sodium Hydroxide | 0.30                |
| Temperature 115°F     |                     |

#### EXAMPLE 4

| Ingredient            | Molar Concentration |
|-----------------------|---------------------|
| Copper Sulfate        | 0.11                |
| Rochelle Salt         | 0.41                |
| Formaldehyde          | 0.80                |
| Potassium Cyanide     | 0.24                |
| Free Sodium Hydroxide | 0.625               |
| Temperature 120°F     |                     |

Plastic articles conditioned, sensitized, and activated as previously described were, following immersion in a strike bath as previously described, immersed in baths having formulations corresponding to each of the foregoing examples and maintained at the temperature indicated as to each. Plastic articles plated in each were provided with highly adherent electroless copper coatings. Upon immersion in the plating bath solution of Examples 1 through 4 of articles having a catalytic noble metal on their surfaces, without first passing such articles through the strike bath, no copper was deposited on the articles.

Through the process of the present invention, a highly stabilized, nonsensitive formulation can be used in the electroless plating bath without significant decomposition over a long period of time. Further, this solution can be used in stainless steel tanks with stainless steel heaters and filters. As a result of the stability imparted to the solution, roughness or so-called "bumps" in the plating deposit are avoided and the electroless plating bath can be operated at elevated temperatures with attendant improvements in production rates economies.

The process and solution of the present invention are also utilizable with articles which, while literally conductive, have conditions or characteristics which prevent application of current of sufficient density to plate satisfactorily by conventional electrolytic plating. This occurs, for example, with respect to pits and depressions in steel articles. The term "nonconductive" as used herein with reference to the practice of the present invention is intended to encompass such conditions or characteristics.

The invention, in its broadest aspects, is not limited to the specific steps and compositions described, and it will be understood that modifications may be made without departing from the scope of the invention as claimed.

We claim:

1. In an electroless plating process, the steps of immersing an article having a catalytic noble metal on its surface in a first electroless plating solution to initiate deposition of the plating metal on the article, removing the article when a thin coating of plating metal has been deposited on the surface of the article, and immersing the article in a second electroless plating solution containing a plating metal electrolessly platable with respect to the plating metal deposited by said first electroless plating solution and having a concentration of an inhibitor which is sufficient to prevent deposition of said plating metal on an article having the catalytic noble metallic surface but does not prevent deposition of said plating metal on an article having the thin coating of plating metal.

2. Process in accordance with claim 1 wherein the article is plastic.

3. Process in accordance with claim 1 wherein the plating metal is copper.

4. In an electroless copper plating process, the steps of immersing an article having a catalytic noble metal on its surface in a first electroless copper plating solution to initiate deposition of copper on the article, removing the article when a thin coating of copper has been deposited on the surface of the article, and immersing the article in a second electroless copper plating solution having a concentration of inhibitor which is sufficient to prevent deposition of copper on an article having the catalytic noble metallic surface but does not prevent deposition of copper on an article having the thin coating of copper.

5. Process in accordance with claim 4 wherein the inhibitor is a water-soluble cyanide.

6. Process in accordance with claim 4 wherein the second electroless copper plating solution is maintained at a substantially constant temperature within the range from 90°F to 140°F.

7. Process in accordance with claim 5 wherein the concentration of cyanide is in the range from 0.0015 to 0.24 moles per liter of solution.

8. Process in accordance with claim 5 wherein the second solution comprises an aqueous solution including from 0.02 M to 0.15 M soluble cupric salt, from 0.03 M to 0.75 M complexing agent for cupric ions, at

least 0.05 M reducing agent, an alkali hydroxide to give a pH in the range from 12 to 14, and from 0.0015 M to 0.24 M water-soluble cyanide.

9. In an aqueous electroless copper plating solution containing cupric ions, a complexing agent for cupric ions, a reducing agent, and a pH adjustor, the improvement which comprises including in said solution a concentration of an inhibitor which is sufficient to prevent deposition of copper on an article having a catalytic noble metallic surface but does not prevent deposition of copper on an article having a thin coating of copper.

10. Solution in accordance with claim 9 wherein the inhibitor is a water-soluble cyanide.

11. Solution in accordance with claim 10 wherein the concentration of cyanide is in the range from 0.0015 to 0.24 moles per liter of solution.

12. Solution in accordance with claim 9 comprising an aqueous solution including from 0.02 M to 0.15 M soluble cupric salt, from 0.03 M to 0.75 M complexing agent for cupric ions, at least 0.05 M reducing agent, an alkali hydroxide to give a pH in the range from 12 to 14, and from 0.0015 M to 0.24 M water-soluble cyanide.

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