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ELECTROLESS PLATING PROCESS

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The present invention relates to plating processes, and and more particularly to a process for electroless plating of a metallic coating on a base member.

Electroless plating processes are well-known in the prior art and provide for the deposition by an autocatalytic chemical reaction of a metal alloy on a suitable surface. In accordance with known electroless plating processes, salts of one or more metals to be plated are dissolved in an aqueous solution adapted to provide a reducing action, and a base member (usually of metal) is then immersed in the solution. A chemical reaction consequently takes place, in which the metal salts are reduced and plated on the base member, the surface of the latter serving to catalyze the reaction. Metallic phosphides are usually deposited, inasmuch as a hypophosphite is usually employed as a reducing agent.

The known electroless plating processes have ordinarily required the use of elevated temperatures for their operation.

Electroless plating processes thus take place in the absence of electric current, and the base members to be plated may be of nonconductive as well as of conductive material, as long as the surfaces thereof provide the necessary catalytic action. If the surface of the base member is "non-active," it may be rendered active by electrodeposition, chemical treatment or other means.

Electroless plating procedures usually insure a uniformity of metallic coating on all of the surfaces being plated. Such uniformity of coating can be obtained along irregular surfaces, edges of base members, and on both interior and exterior surfaces.

As will be realized, electroless plating processes have potential use in the production of components for electrical and electronic devices. The coatings produced should have good characteristics in respect of their hardness and adherence. Also, they must have particular electrical properties, depending upon their desired use (e.g., high conductivity).

It is therefore an object of the invention to provide an improved electroless plating process.

Another object of the present invention is to provide an improved process for the plating of a metallic phosphide coating on a base member.

Another object of the invention is to provide an improved electroless plating process which can be carried out at room temperature.

Another object of the invention is to provide a room-temperature electroless plating process which results in coatings having high conductivity coupled with good characteristics of adherence and hardness.

These and other objects of the invention will become more apparent from the following description thereof.

In carrying out the process of the present invention, a base member such as, for example, an aluminum electrical component is immersed in a plating solution adapted to deposit on the surface thereof a metallic phosphide coating. As a preliminary step, however, the base member should be cleaned and polished for the removal of any grease or oil on the surface thereof. A conventional cleansing agent may here be employed, such as, for example, trichloroethylene vapor. It may in some cases, such as when the base member is of aluminum, be desirable to etch the latter after the cleaning operation. It may also in some cases be desirable to employ conventional electrocleaning means and/or electropolishing means in the cleaning of the base member. As a further preparatory measure, it is usually desirable to immerse the base member in a conventional activating solution, such as, for example, an H_2SO_4 or HCl solution.

The plating solution in which the base member is immersed contains ingredients which may provide a coating of iron phosphide; or of nickel phosphide; or of a phosphide containing nickel in combination with either iron or chromium. The solution contains metallic salt material that is, plating salt adapted to provide the metal ions which will form the desired metallic coating. Thus, a nickel salt or an iron salt may be employed alone; or a nickel salt may be employed in combination with an iron or a chromium salt. Among the suitable salts which may be employed are the chloride, sulphate, acetate, citrate, iodide, bromide, formate, and hydroxide.

As reducing agents, the plating solution contains sodium hypophosphite and formaldehyde. Three complexing agents are also present: i.e., ammonia; a carboxylic acid or salt such as, for example, sodium citrate; and ethylenediaminetetraacetate (E.D.T.A.). The hypophosphite in its reaction in the solution forms a by-product which provides a further reducing action.

After the base member has been immersed in the solution, the latter is maintained by means of ammonium hydroxide at a pH substantially in the range of 9–13. The autocatalytic reaction then proceeds at room temperature.

The base member acts in the nature of a cathode while immersed in the plating solution, and a metallic phosphide coating is deposited thereon. As indicated above, the sodium hypophosphite and formaldehyde serve to reduce the metal salts. The carboxylic complexing agent, the ammonia, and the E.D.T.A. provide a synergistic complexing action; i.e., serve to reinforce the complexing properties of one another. As is well-known, the complexing action prevents the precipitation of undesirable metal compounds.

The carboxylic compound acts in addition as a buffering agent, controlling the pH of the solution. Besides sodium citrate, other examples of carboxylic compounds which may be employed include citric acid, tartaric acid, oxalic acid and salts thereof.

Agitation of the base member cathode is preferred for the obtaining of a uniform coating, especially for base members which are of unusual shape and/or have irregular surfaces, recesses, etc. Ultrasonic or other known types of agitation may be employed for this purpose. The plating solution is also preferably circulated and filtrated by known means during the plating process. The process may be continued for any desired length of time, depending upon the depth of coating desired.

In the case of a base member of a non-active material, conventional special processing prior to the electroless plating procedure may be required. Thus, in the case of copper, the latter should be preliminarily "electroflashed"; i.e., provided with a thin active metallic coating by electroplating, preferably in the electroless solution. Deposits may also be made on glass, resin or other surfaces, which have been rendered active by conventional preliminary chemical treatment.

Example 1

A piece of 1100 series aluminum wire was treated with trichloroethylene vapor in order to remove any grease or oil on the surface thereof. The wire was immersed in the trichloroethylene vapor for fifteen minutes; then heated to 100° C., for one hour; and then again immersed in the trichloroethylene vapor for fifteen minutes. The wire was thereafter etched for about thirty seconds in a commercially available etching solution. After the electropolishing operation, the wire was washed in dis-

tilled water, and thereafter immersed in 20% sulphuric acid at 150° F., for three minutes.

Following the above preliminary treatment, the aluminum wire was immersed in an aqueous plating solution having the following concentrations of salts per 100 ml. solution:

Sodium citrate ($Na_3C_6H_5O_7.2H_2O$)	gr.	17.0
Ferrous sulphate ($FeSO_4.7H_2O$)	gr.	8.4
Nickelous sulphate ($NiSO_4.6H_2O$)	gr.	3.5
E.D.T.A.	gr.	5.0
Sodium hypophosphite ($NaH_2PO_2.H_2O$)	gr.	10.0
Formaldehyde (HCHO)	ml.	20.0

The pH of the above solution was maintained at about 10 by means of additions of 1:1 ammonium hydroxide solution, while the solution remained at room temperature (about 20° C.).

The wire was removed from the plating solution after a period of about forty minutes. The wire then had a hard coating of nickel-iron phosphide, which was found to have good adherence characteristics, and an unusually high conductivity.

Example 2

The procedure of Example 1 was repeated, the wire, however, being immersed in a solution containing 11.9 gr. of ferrous sulphate and no nickelous sulphate (the other ingredients being the same). As a result, a coating of iron phosphide was obtained, which coating exhibited good characteristics in respect of hardness, adherence and conductivity.

Example 3

The procedure of Examples 1 and 2 was again repeated, the plating solution here, however, having been modified so as to contain 11.9 gr. of nickelous sulphate and no ferrous sulphate. As a result, a coating of nickel phosphide was obtained, said coating having the desired above-mentioned qualities in respect of hardness, adherence and conductivity.

Example 4

The general procedure of Examples 1, 2 and 3 was here again followed. However, an aqueous plating solution having the following concentrations of salts per 240 ml. total volume was employed:

Sodium citrate ($Na_3C_6H_7O.2H_2O$)	gr.	34.0
Chromium chloride ($CrCl_3$)	gr.	.2
Nickelous chloride ($NiCl_2$)	gr.	1.0
E.D.T.A.	gr.	10.0
Sodium hypophosphite ($NaH_2PO_2.H_2O$)	gr.	20.0
Formaldehyde (HCHO)	ml.	20.0

A dark, smooth coating of relatively high resistance was obtained, rendering the wire suitable for decorative purposes or for use as an electrical heating element.

Although the invention has been described with reference to particular embodiments thereof, it will be realized that various changes and modifications may be made therein without departing from the spirit of the invention or the scope of the appended claims.

Having thus described the invention, what is claimed and desired to be secured by Letters Patent is:

1. A low temperature process for the electroless plating of a metallic phosphide coating on a base member, said process comprising the steps of immersing the base member in an aqueous solution containing, per 100 milliliters of said solution,

sodium citrate in a concentration of about 17 grams,

sodium hypophosphite in a concentration of about 10 grams,

ethylene diamine tetraacetate in a concentration of about 5 grams,

formaldehyde in a concentration of about 9–20 milliliters,

plating salt selected from the group consisting of ferrous sulfate (about 11.9 grams), a mixture of ferrous sulfate (about 8.4 grams) and nickelous sulfate about 3.5 grams), nickelous sulfate (about 11.9 grams), a mixture of nickelous chloride (about 0.5 gram) and chromium chloride (about 0.1 gram), and

ammonia in an amount sufficient to establish and maintain the pH of said solution at between about 9 and about 13,

maintaining said solution at said pH and at a temperature between about 20° C. and about 23° C. while maintaining said base member in said solution until said base member is coated with said phosphide.

2. The process of claim 1 wherein said mixture of ferrous sulfate and nickelous sulfate is utilized as said plating salt, wherein said formaldehyde is in a concentration of about 20 milliliters per 100 milliliters of said solution and wherein said solution is maintained at about pH 10 and at about 20° C.

3. The process of claim 1 wherein ferrous sulfate is utilized as said plating salt, wherein said formaldehyde is in a concentration of about 20 milliliters per 100 milliliters of solution and wherein said solution is maintained at about pH 10 and at about 20° C.

4. The process of claim 1 wherein nickelous sulfate is utilized as said plating salt, wherein said formaldehyde is in a concentration of about 20 milliliters per said 100 milliliters of said solution, and wherein said solution is maintained at about pH 10 and at about 20° C.

5. The process of claim 1 wherein said mixture of chromium chloride and nickelous chloride is utilized as said plating salt, wherein said formaldehyde is in a concentration of about 9 milliliters per 100 milliliters of said solution and wherein said solution is maintained at about pH 10 and at about 20° C.

References Cited by the Examiner

UNITED STATES PATENTS

2,827,398	3/58	Eisenberg	117—130
2,827,399	3/58	Eisenberg	117—130
2,965,551	12/60	Richaud	117—130
3,024,134	3/62	Nixon	117—130

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