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METHOD OF SILVER PLATING BY CHEMICAL REDUCTION

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This invention relates to electroless plating by the deposition of metals by chemical reduction. More particularly the invention relates to improvement in the deposition of silver from chemical reduction plating solutions.

The chemical reduction process for plating has several advantages over conventional metal electroplating methods. Chemical reduction plating provides a deposit of substantially uniform thickness over articles having complex shapes and other irregularities such as small recesses and apertures. Even the remote surfaces in such recesses may be uniformly plated by the chemical reduction process in contrast with conventional electroplating methods where the plating of such recesses is a practical impossibility. Known prior chemical reduction processes, however, all employ soluble metallic compounds which are exceptionally light sensitive and therefore easily reduced. It will be appreciated that the ease of reduction of such light sensitive salts renders the process difficult to control. Generally in order to achieve control it is necessary to carry out the processes under darkroom conditions or to include other additives in the plating solution which increase the solubility of the compounds and thus reduce the light sensitivity thereof. Attempts to increase the solubility of metallic compounds in aqueous solutions have not been markedly successful and such solutions have, in general, failed to produce a good plate.

It is therefore an object of the instant invention to provide an improved method for plating surfaces with silver by a controllable chemical reduction process.

According to the invention a chemical reduction plating solution is employed in which an insoluble compound of silver is included. Since an insoluble silver compound is employed, the plating reaction is not adversely affected by light and greater control of the plating process is thus obtained. The reduction of the insoluble compound is made possible by including in the plating solution a chelating or complexing soluble compound which forms a soluble complex with the insoluble compound. This complex is then reducible upon a surface by the action of a reducing agent.

Examples of metals and alloys which may be coated or plated with silver by the practice of the present invention include steel, iron, ferrous alloys, nickel, cobalt, gold, silver, platinum, copper, copper base alloys, magnesium, and aluminum. It will be understood that superior silver plating results when the surface of the article to be coated is thoroughly cleaned. Hence, in most instances it is desirable to employ conventional plating pretreatments, such as buffing, abrading, or acid etching prior to chemical reduction plating.

In the practice of a specific embodiment of the invention an improved silver deposit or plating is obtained by immersing an article having a surface to be plated into an aqueous solution in contact with water-insoluble silver cyanide or silver acetate or silver oxide, and containing a reducing agent such as sodium hypophosphite,

and a chelating or complexing agent such as potassium or sodium cyanide. The reduction plating is continued until a predetermined thickness of plating is obtained or until the silver ion content in the solution and the reserve supply of silver cyanide are substantially exhausted. The function of the chelating or complexing agent is to continuously form a soluble complex with a portion of the insoluble silver compound and to continuously hold the silver in solution in a controlled concentration until reduced to the metallic state. During the plating processes the plating solution bath is maintained at a temperature in the range of from about 50° C. to about 110° C. At the higher temperature the plating rate is increased and becomes more difficult to control. Chelating or complexing agents suitable in the chemical reduction plating processes of the instant invention are potassium or sodium cyanide. The reducing agent is preferably the hypophosphite radical which may be introduced as an alkali metal hypophosphite such as sodium or calcium hypophosphite, ammonium hypophosphite, or as hypophosphorous acid.

A chemical reduction plating solution in accordance with the present invention is formed by adding the insoluble silver compound and the soluble chelating or complexing agent to water. The amount of insoluble silver compound is determined by the amount necessary to deposit a desired thickness of silver on a particular surface which amount can, of course, be calculated for a particular article. The ratio of the chelating or complexing agent to the insoluble silver compound is not critical. However, it will be understood that if an ion ratio of greater than about 10 to 1 chelating agent to insoluble compound is employed, the silver ion is held so strongly in solution by the chelating agent that its reduction therefrom becomes difficult and the plating process becomes less controllable. Likewise employing a ratio of less than about 0.1 to 1 chelating agent to insoluble compound results in an extremely low rate of plating or no plating at all since there is an insufficient amount of chelating agent to form a significant amount of soluble complex. The hypophosphite reducing agent is then added to the solution, the quantity being determined by the amount of silver to be reduced. In general it is advisable to provide an excess amount of hypophosphite radical to accommodate side reactions and to maintain the plating reaction during the final reduction stages. It has been found that excellent results are obtainable when an ion ratio of hypophosphite radical to insoluble compound of 0.33–10 to 1 is employed.

The following are illustrative examples of initial plating bath compositions and conditions in accordance with the present invention wherein the quantities, where applicable, are expressed in terms of grams per liter of water:

Example 1

AgCN	2.0
$NaH_2PO_2.H_2O$	10.0
KCN	0.2
Temperature ° C	96.0
pH	13.5
Work load ($cm.^2/cm.^3$)	0.25
Average plating rate ($mgs./cm.^2/hr.$)	5.26

Example 2

AgCN	2.0
$NaH_2PO_2.H_2O$	10.0
KCN	0.2
Temperature ° C	96.0
pH	7.5
Work load ($cm.^2/cm.^3$)	0.25
Average plating rate ($mgs./cm.^2/hr.$)	5.26

Example 3

$AgCN$	20.0
$NaH_2PO_2.H_2O$	100.0
KCN	80.0
Temperature ° C	96.0
pH	13.5
Work load ($cm.^2/cm.^3$)	0.25
Average plating rate ($mgs./cm.^2/hr.$)	6.8

Example 4

$AgCN$	2.0
$NaH_2PO_2.H_2O$	1.0
KCN	0.2
Temperature ° C	96.0
pH	7.1
Work load ($cm.^2/cm.^3$)	0.25
Average plating rate ($mgs./cm.^2/hr.$)	5.0

Example 5

Ag_2O	2.0
$NaH_2PO_2.H_2O$	10.0
KCN	0.1
Temperature ° C	96.0
pH	10.0
Work load ($cm.^2/cm.^3$)	0.25
Average plating rate ($mgs./cm.^2/hr.$)	5.0

Example 6

$AgC_2H_3O_2$	2.0
$NaH_2PO_2.H_2O$	10.0
KCN	0.1
Temperature ° C	96.0
pH	10.0
Work load ($cm.^2/cm.^3$)	0.25
Average plating rate ($mgs./cm.^2/hr.$)	3.6

Example 7

$AgCN$	2.0
$NaH_2PO_2.H_2O$	10.0
$NaCN$	0.4
Temperature ° C	96.0
pH	13.0
Work load ($cm.^2/cm.^3$)	0.25
Average plating rate ($mgs./cm.^2/hr.$)	5.0

It will thus be understood from the foreging description and examples of the invention that an improved method of plating silver by chemical reduction has been provided in which the reduction action is not sensitive to light and is more controllable whereby an improved plating of silver is obtained. It should be understood that, although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited since changes and alterations therein may be made which are within the intended scope of the invention as defined in the claims appended.

What is claimed is:

1. The method of silver-plating comprising the step of contacting a surface to be plated with a plating solution at a temperature in the range of from about 50° to about 110° C., consisting essentially of an alkali metal cyanide, a dissolved hypophosphite reducing agent, dissolved silver ions, and an undissolved silver ion-containing compound in contact with the plating solution, the ion ratio of said hypophosphite ion to the undissolved silver ion being in the range of from about 0.33 to about 10, and the ion ratio of the cyanide ion of the dissolved alkali metal cyanide to the undissolved silver ion being in the range of from about 0.1 to about 10.

2. The method according to claim 1, wherein the undissolved silver compound is silver cyanide.

3. The method according to claim 1, wherein the undissolved silver compound is silver oxide.

4. The method according to claim 1, wherein the undissolved silver compound is silver acetate.

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