

1

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## ELECTROLESS CHROMIUM PLATING

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Our invention relates to both a process in which chromium can be electrolessly deposited on a suitable metallic substrate and to an electroless plating solution used in said process.

The term "electroless deposition of chromium" as known in the art describes a process wherein a metallic substrate is inserted in a bath containing in aqueous solution a chromium salt (such as a chloride or sulphate), a hypophosphate salt (such as sodium hypophosphate), and a suitable buffering (pH controlling) agent (such as sodium acetate). In the ensuing reaction, the chromium is deposited as a pure metal on the surface of the substrate. While the mechanism of this process is not fully understood, it is believed that the hypophosphate ion continuously reduces the dissolved metal salt to the metallic state on the surface of the substrate by means of a catalytic action involving the surface.

It has been found that this reaction, which proceeds in the absence of an externally applied electric field, can take place when the pH of the bath is maintained within the acidic range (as for example a pH of 4-6) or alternatively within the basic range (as for example a pH of 8-10).

This process is defined as electroless plating or deposition to differentiate it from the conventional electroplating or electrolytic deposition technique.

The prior art has knowledge of chromium electroless plating solutions which contain, in aqueous media, sodium hypophosphate, sodium citrate, and a mixture of chromium halides. A chromium electroless deposition produced through the use of this bath proceeds at a deposition rate of about 0.14 mil per hour. Such a rate is too slow and costly for many otherwise desirable commercial applications of this process.

We have invented a new chromium electroless plating solution which, when employed in an electroless plating operation, overcomes this difficulty by sharply increasing the chromium deposition rate.

Accordingly it is an object of the present invention to increase the chromium deposition rate in a chromium electroless plating operation.

Another object is to provide a new and improved chromium electroless plating bath of the character indicated.

Still another object is to provide a new and improved chromium electroless plating bath which incorporates as an essential element a chromium deposition rate controlling agent.

Yet another object is to provide an electroless plating method adapted to deposit chromium at a rate on the order of 2 times higher than that afforded by the aforementioned prior art.

These and other objects of our invention will either be explained or will become apparent hereinafter.

In our invention there is provided a chromium electroless plating solution containing in aqueous media a hypophosphate salt; at least one soluble chromic salt; a

2

buffering agent; and a deposition rate controlling agent soluble in the plating solution.

When the pH of this bath is maintained within an acidic or a basic range, and an electroless plating operation is initiated, chromium deposits out of the solution at a rate on the order of 0.3 mil per hour—an increase of about 100 percent as compared to the known art.

We have used the term chromium deposition rate controlling agent to describe the material whose action in solution results in this extremely rapid rate of deposition. This agent reduces the dissolved chromic ions to the chromous state and also forms a readily reducible complex with the chromous ions; this complex is then rapidly reduced to metallic chromium on the surface of the receiving surface through action of the hypophosphate ion. Thus, any organic or inorganic compound which acts as a combined chromium reducing and chromium complexing agent can be used, providing that this compound is soluble in the plating solution and that the resultant complex can be readily reduced to chromium in the manner indicated. Typical compounds of this type include, for example, oxalic acid and its alkali salts.

All metal substrates which can be electroplated with chromium can be plated in the manner set forth in this application. In this connection, it will be understood that as in conventional chromium plating, the passive metals, such as brass, must be flash coated (i. e. an electrolytic strike) with an extremely thin layer of an active metal, such as nickel, iron, and the like, before a subsequent electroless deposition can ensue.

Our invention will now be explained with reference to the detailed examples which follow.

### Example I

A steel substrate was immersed in an aqueous chromium electroless plating solution having the following composition:

	G./l.
Cr <sub>2</sub> O <sub>3</sub> ·9H <sub>2</sub> O	16
CrCl <sub>3</sub> ·6H <sub>2</sub> O	1
Sodium acetate	10
Sodium hypophosphate	10
Potassium binoxalate	4.5

The bath was maintained at a temperature within the range 75°-90° C. and at a pH falling within the range 4-6. It was found that a dense, adherent, non-porous chromium layer was formed on the substrate surface and that the deposition rate was approximately 0.3 mil per hour.

A brass disc was flash coated (that is, a "strike" coating) with nickel and then immersed in the same solution. The same operating conditions were established and the results were substantially identical.

### Example II

A brass disc was flash coated with nickel and then immersed in an aqueous chromium electroless plating solution having the following composition:

	G./l.
CrBr <sub>3</sub> ·9H <sub>2</sub> O	16
CrI <sub>3</sub> ·9H <sub>2</sub> O	1
Sodium citrate	10
Sodium hypophosphate	10
Sodium binoxalate	9.0

The bath was maintained at a temperature within the range 75°-90° C. and at a pH falling within the range 8-10. The results were substantially identical with Example I.

A steel substrate was immersed in the same solution. The same operating conditions were established and the results were substantially the same.

While we have shown and pointed out our invention as applied above, it will be apparent to those skilled in the art that many modifications can be made within the scope and sphere of our invention as defined in the claims which follow.

What is claimed is:

1. An electroless chromium plating solution composed of the following in aqueous solution: a hypophosphite salt having a concentration of about 10 grams per liter; a buffering agent; at least one chromic salt having a concentration of about 17 grams per liter; and a chromium deposition rate controlling agent soluble in the solution and characterized by the ability to reduce chromic ions to chromous ions and to form a readily reducible complex with said chromous ions, said agent being selected from the group consisting of oxalic acid and its alkali salts, said agent having a concentration falling within the approximate range 4.5-9.0 grams per liter.

2. An electroless chromium plating solution composed of the following in aqueous solution: a hypophosphite salt having a concentration of about 10 grams per liter; a buffering agent; at least one chromic salt having a concentration of about 17 grams per liter; and a chromium deposition rate controlling agent soluble in the solution and characterized by the ability to reduce chromic ions to chromous ions and to form a complex with said chromous ion readily reducible to metallic chromium under electroless catalytic action, said agent being selected from the group consisting of oxalic acid and its alkali salts, said agent having a concentration falling within the approximate range 4.5-9.0 grams per liter.

3. A method for chromium plating an active metal substrate which comprises the step of immersing said substrate in an electroless chromium plating solution composed in aqueous solution of a hypophosphite salt having a concentration of about 10 grams per liter; a buffering agent; at least one chromic salt having a concentration of about 17 grams per liter; and a chromium deposition rate controlling agent soluble in the solution and characterized by the ability to reduce chromic ions to chromous ions and to form a readily reducible complex with said chromous ion, said agent being selected from the group consisting of oxalic acid and its alkali salts, said agent having a concentration falling within the approximate range 4.5-9.0 grams per liter, whereby said substrate is chrome plated through electroless plating action.

4. A method for producing a chromium electroless plating bath which comprises the steps of dissolving a chromium deposition rate controlling agent into an aqueous solution containing a hypophosphite salt having a concentration of about 10 grams per liter, a buffering agent, and at least one chromic salt having a concentration of about 17 grams per liter, said rate controlling agent being selected from the group consisting of oxalic acid and its alkali salts, said agent having a concentration falling within the approximate range 4.5-9.0 grams per liter; reacting said rate controlling agent with said chromic ions to reduce said chromic ions to chromous ions and to form a complex with said chromous ions, said complex being easily reducible to metallic chromium in the presence of the hypophosphite ion on a suitably prepared substrate surface.

5. An electroless chromium plating solution composed of the following in aqueous solution: a hypophosphite salt having a concentration of about 10 grams per liter; a buffering agent having an acidic pH value; at least one chromic salt having a concentration of about 17 grams per liter; and a deposition rate controlling agent soluble

in the solution and characterized by the ability to reduce chromic ions to chromous ions and to form a complex readily reducible to metallic chromium under electroless catalytic action, said agent being selected from the class consisting of oxalic acid and its alkali salts, said agent having a concentration falling within the approximate range 4.5-9.0 grams per liter and salts of these acids.

6. An electroless chromium plating solution composed of the following in aqueous solution: a hypophosphite salt having a concentration of about 10 grams per liter; a buffering agent having a basic pH value; at least one chromic salt having a concentration of about 17 grams per liter; and a chromium deposition rate controlling agent soluble in the solution and characterized by the ability to reduce chromic ions to chromous ions and to form a complex with said chromous ion readily reducible to metallic chromium under electroless catalytic action, said agent being selected from the class consisting of oxalic acid and its alkali salts, said agent having a concentration falling within the approximate range 4.5-9.0 grams per liter.

7. A method for chromium plating an active metal substrate which comprises the step of immersing said substrate in an electroless chromium plating solution composed in aqueous solution of a hypophosphite salt having a concentration of about 10 grams per liter; a buffering agent; at least one chromic salt having a concentration of about 17 grams per liter; and a chromium deposition rate controlling agent soluble in the solution; said agent reducing the chromic ions to chromous ions and forming a readily reducible complex with said chromous ions, said complex at the surface of said substrate being reduced to metallic chromium by the hypophosphite ion, said agent being selected from the group consisting of oxalic acid and its alkali salts, said agent having a concentration falling within the approximate range 4.5-9.0 grams per liter.

8. The method as set forth in claim 7, wherein said active metal substrate is composed of a passive metal base and an outer coating of an active metal bonded to said base.

9. A method for chromium plating an active metal substrate which comprises the steps of dissolving a chromium deposition rate controlling agent into an aqueous solution containing a buffering agent, a hypophosphite salt having a concentration of about 10 grams per liter and at least one chromic salt having a concentration of about 17 grams per liter, said controlling agent reducing the chromic ions to chromous ions and forming a readily reducible complex with said chromous ions, said agent being selected from the group consisting of oxalic acid and its alkali salts, said agent having a concentration falling within the approximate range 4.5-9.0 grams per liter; and inserting said substrate into said complex containing solution, the hypophosphite ion reducing said complex to metallic chromium at the surface of said substrate.

10. The method as set forth in claim 9, wherein the solution is maintained at a pH within the range 4-6, and the temperature of the solution is maintained within the range 75°-90° C.

11. The method as set forth in claim 9, wherein the solution is maintained at a pH within the range 8-10, and the temperature of the solution is maintained within the range 75°-90° C.

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