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ELECTROLESS IRON PLATING

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

The term "electroless deposition" as known in the art describes a process wherein a metallic substrate is inserted in a bath containing in aqueous solution a salt (such as a chloride or sulfate) of a metal selected from the group composed of nickel, cobalt and chromium, a hypophosphite salt (such as sodium hypophosphite) and a suitable buffering (pH controlling) agent (such as sodium acetate). In the ensuing reaction, the nickel, cobalt or 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 hypophosphite 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 4-6) or alternatively within the basic range (as for example 8-10).

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

Cobalt and nickel are both members of the same group in the periodic table. Since iron is also a member of this group, it has been assumed that iron could also be deposited through use of this electroless deposition technique. However, while I know that attempts to deposit iron in this manner have been made, I do not know of any such attempts which have been successful. For example, when a ferrous salt, such as ferrous sulfate, is substituted for a nickel or cobalt salt in the bath previously described, it will be found that the iron will precipitate from the bath in the form of ferrous hydroxide and no electroless deposition will occur.

In my investigations on this process, I have succeeded in developing a new type of electroless plating solution, and I have further discovered that I can electroless deposit iron through use of this new composition.

Accordingly, it is an object of the present invention to provide a new and improved electroless plating solution.

It is another object of the invention to provide a new and improved process for the electroless deposition of iron.

Still another object is to provide a new and improved electroless plating solution adapted for the electroless deposition of iron which incorporates organic iron sequestering agents which prevent the formation of ferrous hydroxide and thus permit the electroless deposition to proceed successfully.

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

The buffering agent in a conventional electroless plating bath serves to regulate the pH of the solution by preventing rapid changes in pH values. In my invention,

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this buffering agent is replaced by at least one organic acid or a monobasic or polybasic salt of this acid which not only provides a buffering action but also acts as a sequestering or chelating agent. Stated differently, this organic salt not only regulates the pH in the usual manner but also forms a complex with the positive metal ion which prevents the undesired side reactions. Specifically when a ferrous salt is incorporated into the bath, the complex formed between the ferrous ion and the buffering and sequestering agent or agents prevents the formation of ferrous hydroxide and permits the electroless deposition to proceed.

The agent is only effective in a basic plating solution; I have obtained excellent results when the pH of the solution was held within the range 8-10.

My process can be used to plate iron on any metal substrate which can be electrolytically plated with iron. In this connection it should be understood that the passive metal substrates which must be activated through application of a thin flash coating (that is an electrolytic "strike") of an active metal, such as silver or iron before an electrolytic deposition can ensue, must likewise be flash coated before an electroless plating operation can ensue.

My invention will now be described in detail with reference to the detailed examples which follow.

Example I

An electroless bath was prepared containing the following ingredients in aqueous solution:

	Grams/liter
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ -----	30
NaH_2PO_2 -----	10
$2\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 11\text{H}_2\text{O}$ -----	100

A nickel substrate was inserted into the bath. The pH of the bath was held within the range 8-10 and the temperature was held within the range 75-90° C. It was found that an iron coating was deposited on the nickel. This coating had a matte surface and was found to be non-porous and extremely adherent to the substrate. The deposition rate was found to be approximately 0.5 mil per hour.

Example II

An electroless bath was prepared containing the following ingredients in aqueous solution:

	Grams/liter
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ -----	30
NaH_2PO_2 -----	10
$\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ -----	50

A brass substrate which had previously received an iron strike (applied in conventional manner) was inserted into the bath. The bath temperature and pH were adjusted as in Example I, and it was found that the brass substrate was coated with iron in the same manner as in Example I.

Example III

Example I was repeated using an aqueous electroless bath having the following composition:

	Grams/liter
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ -----	30
NaH_2PO_2 -----	10
$\text{Na}_2\text{C}_2\text{O}_4$ -----	25

The results were substantially identical with those obtained in Example I.

While I have shown and pointed out my 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 my invention as defined in the claims which follow.

What is claimed is:

1. The method for electrolessly depositing an iron coating on the surface of a metallic substrate, which comprises the steps of inserting said substrate into an electroless plating bath consisting essentially of an aqueous solution containing at least one ferrous salt having a concentration of approximately 30 grams per liter, a hypophosphite salt having a concentration of approximately 10 grams per liter, and at least one buffering and sequestering agent soluble in the bath, said agent being selected from at least one element of the group consisting of oxalic acid and its salts, citric acid and its salts and Rochelle salts, the concentration of said agent falling within the approximate range 25-100 grams per liter; and maintaining the pH of said bath in the basic region until the electroless deposition is carried to completion.

2. A method for preparing an iron electroless deposition solution which comprises the steps of introducing at least one buffering and iron sequestering agent into an aqueous solution consisting essentially of at least one ferrous salt having a concentration of approximately 30 grams per liter and a hypophosphite salt having a concentration of approximately 10 grams per liter; and maintaining said solution in the basic region, said agent sequestering the ferrous ions and thereby preventing ferrous hydroxide formation, said agent being selected from at least one element of the group consisting of oxalic acid and its salts, citric acid and its salts and Rochelle salts, the concentration of said agent falling within the approximate range of 25-100 grams per liter.

3. An electroless plating bath consisting essentially of, in aqueous solution, at least one ferrous salt having a concentration of approximately 30 grams per liter; a hypophosphite salt having a concentration of approximately 10 grams per liter; and at least one buffering and sequestering agent soluble in the bath, said agent being

selected from at least one element of the group consisting of oxalic acid and its salts, citric acid and its salts and Rochelle salts, the concentration of said agent falling within the approximate range 25-100 grams per liter, said bath being maintained at a pH within the range 8-10 and at a temperature within the range 75°-90° C., said agent sequestering the ferrous ions to prevent the formation of ferrous hydroxide.

4. The method for electrolessly depositing an iron coating on the surface of a metallic substrate, which comprises the steps of inserting said substrate into an electroless plating bath consisting essentially of an aqueous solution containing at least one ferrous salt having a concentration of approximately 30 grams per liter, a hypophosphite salt having a concentration of approximately 10 grams per liter, and at least one buffering and sequestering agent soluble in the bath, said agent being selected from at least one element of the group consisting of oxalic acid and its salts, citric acid and its salts and Rochelle salts, the concentration of said agent falling within the approximate range 25-100 grams per liter; and maintaining the pH of said bath in the range 8-10 until the electroless deposition is carried to completion, said agent sequestering the ferrous ions to prevent the formation of ferrous hydroxide.

5. The method as set forth in claim 4 wherein said bath is held at a temperature within the range 75°-90° C.

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