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ELECTROLESS DEPOSITION OF IRON ALLOYS

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My invention relates both to a process in which iron and at least one metal from the group composed of cobalt, nickel, and chromium 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.

In my copending application, Serial No. 561,670, filed January 26, 1956, I disclosed an electroless plating solution and a process utilizing this solution to electrolessly deposit iron on the surface of a suitable substrate.

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 the above identified application, 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; excellent results were obtained when the pH of the solution was held within the range 8-10.

The 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 nickel or iron must likewise be flash coated before an electroless plating operation can ensue.

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In my investigations in the above process, I have succeeded in developing additional new types of electroless plating solutions and I have further discovered that I can electrolessly co-deposit iron together with at least one metal from the group composed of nickel, cobalt and chromium out of such solutions onto the surface of a metal substrate.

Accordingly, it is an object of the present invention to provide new and improved electroless plating solutions of the character described.

It is another object of the invention to provide a new and improved process for the electroless codeposition of iron with at least one metal selected from the group composed of nickel, cobalt and chromium.

Still another object is to provide a new and improved electroless plating solution adapted for the electroless codeposition of iron with at least one metal selected from the group composed of nickel, cobalt and chromium, which incorporates organic sequestering and reducing agents which prevent the formation of hydroxides of the deposited metals and thus permits the electroless deposition to proceed successfully.

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

The electroless codeposition is accomplished by utilizing those salts of the metals to be codeposited which are soluble in a basic plating solution and in which the metallic ions exist in the lowest valence state. The basic plating solution in addition to these metallic salts and the hypophosphite salt, must also contain at least one organic acid or a monobasic or polybasic salt of this acid.

Such organic salts and acids have these different functions: they provide the conventional buffering action; they serve as reducing agents to maintain the ions of the metals to be codeposited in their lowest valence states; they sequester the ions of the metals to be codeposited to form one or more complexes with these ions which prevent undesirable side reactions as for example the formation of insoluble hydroxides. Thus, such salts and acids are buffering, reducing and sequestering agents.

The codeposited metals deposit out of this solution in the form of an alloy.

In the same fashion as indicated previously in the above mentioned copending application, this process can be used to plate the alloy on any metal substrate which can be electrolytically plated; passive metal substrates must be activated in conventional manner before an electroless deposit 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
FeSO ₄ ·7H ₂ O	30
NaH ₂ PO ₂	10
2Na ₂ C ₆ H ₅ O ₇ ·11H ₂ O	100
60 NiSO ₄ ·7H ₂ O	30
NaKC ₄ H ₄ O ₆ ·4H ₂ O	60

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 iron-nickel alloy coating containing about equal parts by weight of iron and nickel 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 0.4 mil per hour.

Example II

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

	Grams/liter
FeSO ₄ ·7H ₂ O	30
NaH ₂ PO ₂	10
NaKC ₄ H ₄ O ₆ ·H ₂ O	50
CoSO ₄ ·7H ₂ O	10

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 an iron-cobalt alloy in the same manner as in Example I. This alloy contained about 70% by weight of iron and about 30% by weight of cobalt.

Example III

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

	Grams/liter
FeSO ₄ ·7H ₂ O	30
NaH ₂ PO ₂	10
CrCl ₃ ·6H ₂ O	10
Na ₂ C ₂ O ₄	50
NaKC ₄ H ₄ O ₆ ·4H ₂ O	60

The results were substantially identical with those obtained in Example I except that the deposited alloy in this example was an iron-chromium alloy containing approximately 90% by weight of iron and approximately 10% by weight of chromium.

Example IV

Example I was repeated using a nickelous sulphite containing about 0.1% by weight of cobaltous sulphate. The resultant deposited alloy was formed to contain approximately 50% by weight of iron, 49.9% by weight of nickel and 0.03% by weight of cobalt.

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 alloy on the surface of a metallic substrate, which comprises the steps of inserting said substrate into an electroless plating bath consisting of an aqueous solution containing a ferrous salt together with a salt of at least one metal from the group composed of cobalt, nickel and chromium, the positive metal ions being present in their lowest ionic valence state, said ferrous salt and said one metal salt having a combined concentration falling within the approximate range 40-60 grams per liter, the ferrous salt concentration being at least 50% by weight of said combined concentration; a hypophosphite salt having an approximate concentration of about 10 grams per liter; and at least one buffering, sequestering and reducing 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 50-160 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, sequestering and reducing 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 50-160 grams per

liter into an aqueous solution containing at least one ferrous salt together with at least one positive ion selected from the group consisting of nickel, cobalt and chromium, said positive ion being in its lowest valence state, the source of said ferrous ion and the source of said one metal having a combined concentration falling within the approximate range 40-60 grams per liter, the ferrous source concentration being at least 50% by weight of said combined concentration, and a hypophosphite salt having an approximate concentration of about 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 the class composed of the organic acids and the monobasic and polybasic salts of these acids.

3. An electroless plating bath containing in aqueous solution at least one ferrous salt together with a salt of at least one metal from the group consisting of cobalt, nickel and chromium, the positive metal ions being present in their lowest ionic valence state, said ferrous salt and said one metal salt having a combined concentration falling within the approximate range 40-60 grams per liter, the ferrous salt concentration being at least 50% by weight of said combined concentration; a hypophosphite salt having an approximate concentration of about 10 grams per liter; and at least one buffering, sequestering and reducing agent soluble in the bath, said agent being selected from at least one element of the groups 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 50-160 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 positive ions to prevent the formation of insoluble hydroxides.

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 composed of an aqueous solution containing at least one ferrous salt, together with a salt of at least one metal from the group consisting of cobalt, nickel and chromium, the positive metal ions being present in their lowest ionic valence state, said ferrous salt and said one metal salt having a combined concentration falling within the approximate range 40-60 grams per liter, the ferrous salt concentration being at least 50% by weight of said combined concentration; a hypophosphite salt having an approximate concentration of about 10 grams per liter; and at least one buffering, sequestering and reducing 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 50-160 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 ions of the metals to be deposited to prevent the formation of insoluble hydroxides.

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

References Cited in the file of this patent

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