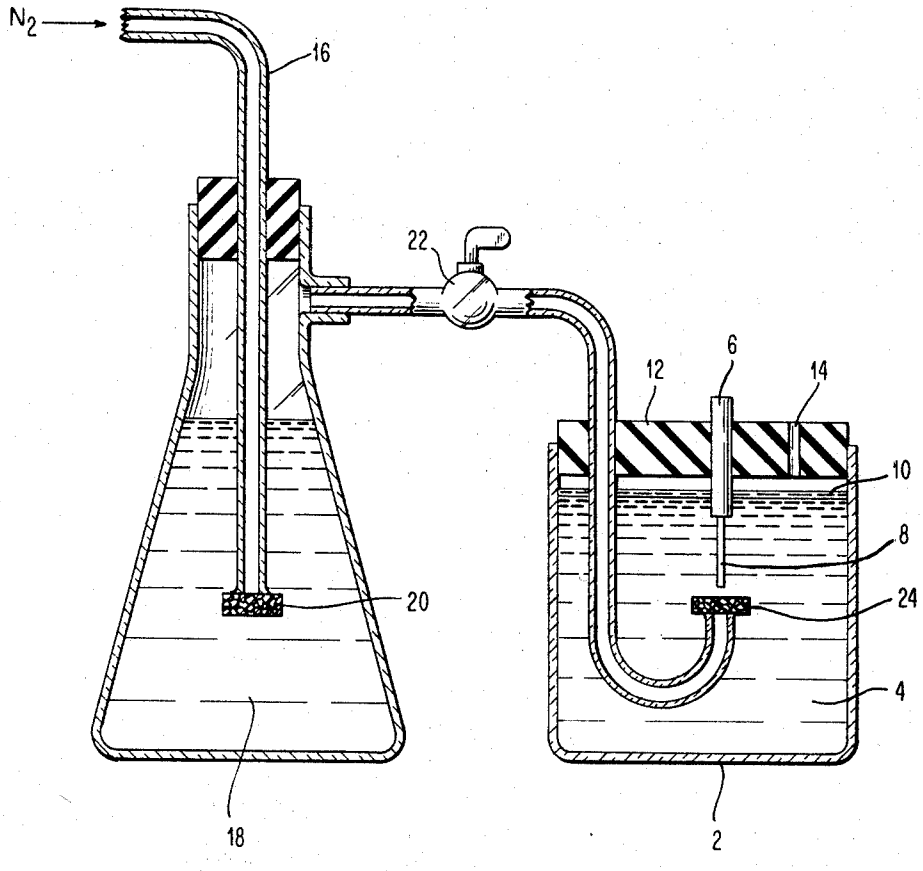
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ELECTROLESS Ni - F DEPOSITION PROCESS

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ELECTROLESS Ni-Fe DEPOSITION PROCESS

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ABSTRACT OF THE DISCLOSURE

An iron or iron-nickel electroless deposition bath's useful life is prolonged by preventing the oxidation thereof. The bath is purged by a finely dispersed stream of nitrogen gas bubbles, prior and subsequent to the addition of ferrous ions to the bath. The nitrogen gas, prior to entering the electroless bath, is passed through a solution whose pH and temperature are the same as that of the bath. Both the solution and bath contain a common volatile base, so that the volatilized base of the bath is continuously replenished therein. The purging nitrogen gas also agitates the bath and results in a film free of oxide occlusions.

This invention relates to a process in which iron or nickel-iron alloys can be electrolessly deposited onto a suitable conducting substrate, and more particularly to a process for increasing the useful life of the bath in which said electroless deposition takes place.

The term "electroless deposition" as known in the art describes a process wherein a conducting substrate is inserted in a bath containing, in aqueous solution, a salt, such as a chloride or sulfate, of a metal such as iron, nickel, cobalt and chromium, a reducing agent, such as sodium hypophosphite, a suitable complexing agent such as sodium citrate or sodium potassium tartrate and a buffering agent where needed. In the ensuing reaction, the iron, nickel, cobalt or chromium is deposited as a pure metal on the surface of the substrate. Other baths permit alloys of iron and nickel to be plated onto a suitable substrate. The art of electroless plating has been given extensive treatment in a publication entitled, "Symposium on Electroless Nickel Plating (Catalytic Deposition of Nickel-Phosphorus Alloys by Chemical Reduction in Aqueous Solution)," identified as ASTM Special Technical Publication No. 265 and published by the American Society for Testing Materials in Philadelphia, Pa., in 1959.

Electroless iron and electroless iron-nickel alloys are plated from an alkaline bath. Iron and nickel in these baths are kept from precipitating as hydroxides by complexing the metallic ions with suitable complexing agents. When all of the factors in the bath are kept constant, the percent of iron in the alloy, as well as the bath life, depends on the ratio Fe(II)/Ni(II) in the bath. Since Fe(II) oxidizes rapidly to Fe(III) in alkaline solutions, it becomes difficult to control the rate of deposition and percent of Fe that will be plated on a substrate held within such bath. It is also noted that $(H_2PO_2)^-$ becomes oxidized and, as its concentration is changed, the rate of deposition of Ni-Fe changes.

The present invention prevents or considerably slows down the oxidation mentioned above by purging the bath, prior to the addition of the ferrous salt to the bath as well as throughout the life of the bath, with a continuous, finely dispersed stream of nitrogen gas bubbles. The nitrogen gas, prior to entering the electroless bath, is passed through a solution whose pH and temperature are the same as that of the bath. Where, for example, the bath contains ammonia, the nitrogen gas is bubbled through an ammoniacal water solution whose pH and temperature, the latter being the main controllers of the activity of the volatile constituents, which in the instant case are NH_3 and H_2O, are nearly the same as that of the bath. In short, where a bath contains a pH controller that is volatile, the purging nitrogen passes through a solution containing such volatile constituent.

While the theory of operation of the electroless process is not always clearly understood, it has been observed that the life of the bath used in an electroless deposition where iron deposition is involved is shortened due to a high oxidation of the iron and a bath having a high pH. Since iron and nickel-iron alloys are electrolessly deposited in an alkaline source, ergo, a high pH, there is a strong tendency for the oxidation of the iron and $(H_2PO_2)^-$. It is this oxidation which must be avoided in order to extend the life of such bath. By passing nitrogen through a chamber containing ammonium hydroxide, finely dispersed nitrogen will entrain the ammonia and carry it to the plating bath where its presence compensates for loss of the pH controlling factor, namely, the ammonium hydroxide in the bath. The purging nitrogen also agitates the bath solution and results in a film free of oxide occlusions.

It is an object of this invention to provide a new and improved process for the electroless deposition of iron and iron-nickel alloys.

It is yet another object to provide a new and improved process for extending the useful life of a bath employed in the electroless iron and iron-nickel alloy deposition.

It is a further object to improve electroless deposition processes by stabilizing the bath composition employed in such processes.

It is yet another object to attain uniform composition through the thickness of the deposited film.

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of a preferred embodiment of the invention as illustrated in the accompanying drawing.

The sole figure illustrates a means for carrying out the objects set forth hereinabove. As seen in the sole figure a container **2** houses a suitable plating solution **4**, generally alkaline, and element **6** is a support for holding an item **8** to be placed within the solution **4**. A cover **10** comprises a layer of inert, organic material, such as silicon oil or xylene, the latter serving to slow down the oxidation rate of the bath. An additional cover **12** serves to cut down the evaporation rate of the plating solution and an opening **14** is provided in such cover for the escape of gases to relieve pressure of expansion.

Nitrogen gas N_2, or other inert gas, is fed through tube **16** into a solution of NH_4OH and the nitrogen is dispersed into a fine stream of gas bubbles by passing such nitrogen gas through fritted glass **20** before entering the ammonia solution **18**. The ammoniated nitrogen passes through valve **22** and enters the plating solution after passing through another fritted glass exit port **24**.

Representative plating solutions are composed of:

(A)

$NiCl_2 \cdot 6H_2O$	g./l.	14
$Fe(NH_4)_2(CO_4)_2 \cdot 6H_2O$	g./l.	10.3
$KnaC_4H_4O_6 \cdot 4H_2O$	g./l.	35
$NaH_2PO_2 \cdot H_2O$	g./l.	6
NH_4OH	ml./l.	230

(B)

Nickel chloride	g./l.	14.0
Ferrous ammonium sulfate	g./l.	6.5
Rochelle salt	g./l.	32.5
Sodium hypophosphite	g./l.	4.4
Ammonium hydroxide	m./l.	230

The NH_4OH chosen for solution 18 was maintained at 55°–75° C. so that a pH of 11.5 could be maintained. When another plating solution composed of

(C)

	G./l.
$NiCl_2 \cdot 6H_2O$	15
$FeCl_2 \cdot 4H_2O$	33.17
$NaH_2PO_2 \cdot H_2O$	10
NH_4Cl	50
$Na_3C_6H_5O_7 \cdot 2H_2O$	100

was used, 28 ml./l. of NH_4OH was used to make the pH 8.2 at the plating temperature of the bath. The nickel chloride serves as the source of nickel and the ferrous ammonium sulfate is the source of iron and also serves as a buffer. The tartrate or Rochelle salt is the complexing agent and the sodium hypophosphite is the reducing agent. The ammonium hydroxide is the controller or determinant of the pH of the bath solution and also serves to complex nickel.

The nitrogen entering at **16** exits from fritted member **20** as finely dispersed bubbles, the latter entraining the ammonia from solution **18** and such ammoniated nitrogen, whose rate of entry into the bath is regulated by valve **22**, is further dispersed by fritted member **24** before entering the bath solution **4**. The finely dispersed bubbles not only agitate the bath at the deposition surface of sample **8**, but also sweeps out any oxidating agent in the bath **4** and forms a protective atmospheric layer under cover **12**. Of course, the ammonia added to bath **4**, replaces the highly volatile ammonia that escapes through port **14**, such replacement being necessary to maintain the pH of the bath solution **4**. Other known alkaline baths, employed in the electroless deposition of iron and nickel-iron, can have their lives extended so long as the nitrogen or other inert gas is employed to entrain that volatile substance in solution **18** which is employed in bath **4** to preserve the pH of the bath solution.

Although the purging feature is a primary way of extending the life of electroless Fe and electroless Ni-Fe baths and to provide uniform composition free of oxide occlusions in the films, certain other practical considerations will help to extend the life of such baths. It is recommended that the ratio of bath volume 4 to exposed surface area of the bath be high. Moreover, the cover **12** should have a tight seal so that the space above the xylene or silicon oil cover is filled primarily with nitrogen and ammonia vapor in addition to the water vapor and hydrogen gas being produced during the chemical reactions taking place within the bath **4** so as to further avoid the presence of oxygen.

While the invention has been shown and described with reference to a preferred embodiment thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A method of extending the life of an electroless bath containing metal ions selected from iron and iron-nickel ions, hypophosphite reducing agents and a volatile base comprising the steps of passing an inert gas through an ammonium solution whose activity of its volatile constituents is the same as said electroless bath, and then passing said gas through said bath.

2. A method according to claim **1** wherein said bath contains iron ions and said inert gas is passed through an ammonium solution whose pH and temperature are the same as said electroless bath, and then passing said gas through said bath.

3. A method according to claim **1** wherein said inert gas is nitrogen.

4. A method according to claim **1** wherein said volatile base is ammonium hydroxide.

5. A method of extending the life of an electroless alkaline bath comprising iron ions, hypophosphite reducing agent and a volatile pH controller comprising the steps of passing nitrogen gas through an ammonium solution whose pH is the same as said electroless bath and which contains the pH controller of said bath, and then passing said nitrogen through said bath.

References Cited

UNITED STATES PATENTS

2,819,188	1/1958	Metheny et al.	117—130
2,938,805	5/1960	Agens	117—130 X
3,261,711	7/1966	Sallo	117—130 X
3,281,266	1/1966	Colonel	117—130

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