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ELECTROLESS PLATING OF METALS

Wayne Martin Fassell, Jr., Newport Beach, Hugh C. Boyd, Capistrano Beach, and Albert M. Saul, Los Alamitos, Calif., assignors to The Ford Motor Company, Dearborn, Mich., a corporation of Delaware
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This invention relates to electroless processes for plating metals, and more particularly to an improved process for the plating of metallic surfaces with a coating of nickel by autocatalytic chemical reduction reaction.

The electroless deposition of nickel is a process for the coating of metallic surfaces with nickel by chemical reaction without the use of electricity. A nickel coating is deposited uniformly over metal objects of irregular shape even in the deepest of recesses. Consequently, the process has been finding increased commercial utilization because it can accomplish plating operations which are impossible by conventional electrodeposition methods.

While the electroless process has important advantages over electroplating processes in such aspects as uniformity of coating, corrosion resistance, and in general, overall improved characteristics of the coating, the electroless process has a tendency to slow down with the deposition rate rapidly decreasing from the beginning until the end of the plating process. The rate of deposition is ordinarily too slow for many commercial applications, and in many instances the deposition rate decreases in two to five minutes to virtually zero, thereby limiting the coating thickness to 0.0001" or less. In order to start the electroless process again, it is necessary to replace the bath or add significant amounts of ingredients thereto. Additionally, dropouts and pitting often incur during plating by electroless processes.

In an electroless process the hypophosphite ingredient is gradually exhausted. Because of this, less deposit is secured during each successive unit interval of time. Even if hypophosphite is added in strength, the process is effectively inhibited by too great a concentration of phosphite and therefore the bath must be discarded. Additionally, as the substrate is covered with the nickel coating, the catalytic effect of the substrate in the process is impaired thereby further slowing down the deposition rate. Accordingly, it is an object of this invention to provide an electroless plating process of continuous and faster deposition rates.

The process of this invention contemplates an electroless deposition process the uniformity of whose rate is materially aided by the addition of superimposed direct current pulses at periodic intervals. The addition of the pulsating direct current provides for both a substantial increase in the rate of plating obtainable and also diminishes the tendency of the bath to exhaust the hypophosphite. Because of the improved rate of deposition and characteristics of the bath, a film thickness up to .005" may be obtained without changing the bath. A uniform coating relatively free of pinholes and scratches may be realized.

It is therefore another object of this invention to provide an improved electroless process for the deposition of nickel.

It is still another object of this invention to provide an electroless deposition process whereby a much greater rate of deposition may be achieved.

It is a further object of this invention to provide an electroless deposition process of faster rate and improved bath characteristics.

Other objects of the invention will become apparent from the following description read with the appended claims.

According to a material feature of the electroless process of this invention, an electroless deposition process is achieved which is applicable to the plating of nickel on metals such as steel, iron, nickel, cobalt, copper, or copper base alloys. In advance of the plating process, the metallic objects to be plated are preferably cleaned by any conventional procedure and then given a conventional acid dip. Objects of steel, iron, and nickel, having been cleaned and acid-dipped, are ready for immersion in a plating bath. Objects of copper and copper base alloys should be given additional preplating treatment in the form of a momentary bright acid dip followed by a dip for about one minute in a solution of palladium chloride. The objects to be plated may be suspended in the plating bath by a string.

According to the basic electroless plating process, which is well known in the art, and may be found, for example, in the United States Patent No. 2,532,283 to Brenner and Riddell, electroless plating without the use of electric current is accomplished by utilizing a bath having an aqueous solution of the nickel salt and containing a relatively low concentration of hypophosphite. In the bath, the electroless process involves the reduction of hot nickel chloride salt solutions with sodium hypophosphite. Citric acid is added to the bath as a combined buffering and complexing agent. The reaction utilizes about one third of the hypophosphite reducing power because of a concurrent reaction between the hypophosphite and water to produce hydrogen and phosphite. Thus, the nonelectrolytic nickel deposits are not pure nickel but consist of a nickel phosphorus alloy containing from two to ten percent phosphorus. These deposits are generally much harder than the electrodeposit of pure nickel. The general process condition involves a bath composition wherein is included nickel chloride, ammonium chloride, sodium citrate, and sodium hypophosphite. The concentration of nickel may be thirty grams per liter, the concentration of ammonium chloride may be fifty grams per liter, the concentration of sodium citrate 100 grams per liter, and the concentration of sodium hypophosphite ten grams per liter.

The pH of the solution strongly controls the deposition rate of the nickel. The most satisfactory pH range for optimum nickel deposition is between 8.5 and 9.4 with an optimum range of between 9.0 and 9.2. However, the pH may be as high as 10. Since the pH control is critical, the bath must be monitored and corrected as required to maintain the proper pH. This may be accomplished by the addition of ammonium hydroxide in a continuously recirculating system. The temperature of the bath appears to have no significant effect upon the alloy composition, but seriously affects the deposition rate. Deposition rates at solution temperatures below 92° centigrade are negligible. At temperatures in excess of 100° centigrade, the solution may become unstable so as to spontaneously reduce the metals from the solution. For this reason, the preferred temperature of the bath is in the range of between 93 and 95° centigrade with 94° centigrade found to be an ideal temperature. Because of the relatively high temperature involved and the narrow range of pH which is allowable, it may be necessary to add large quantities of ammonium hydroxide during the plating process.

Although the presence of an electric current during the plating is not necessary to an electroless process, according to the invention, the application of a small current applied in intervals of a few seconds and of a low level substantially increases the deposition rates as compared to the completely nonelectrolytic operation of known electroless plating processes. A D.C. pulse current with a range of current density from 0.1 to 10 amps per square foot, and at a current duration of one

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to ten seconds pulse each minute, is applied to the bath to aid the electroless plating process. In applying this current, the metallic objects undergoing electroless plating are poled cathodically. The application of the electric current does not produce a conventional electro-
deposition of nickel on the metallic objects undergoing electroless plating since the current density is about one-tenth of the normal current required for known electro-
deposition processes and the duty cycle of the applied current is about one-sixth.

The primary effect of the addition of a D.C. pulse current to the electroless process is to effect a restarting of the electroless process which has slowed down due to the normal characteristics of an electroless process. As noted hereinbefore, in known electroless plating processes, as the process continues and the nickel is deposited on the cathode, the decomposition of the sodium hypophosphite tends to block the process by preventing the discharge of hydrogen from the cathode which is essential to the deposition of the nickel on the material. Therefore, because of the gradual exhaustion of the hypophosphite which leads to a decreasing release of hydrogen ions from the plating material, less deposit of nickel is secured during

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bath at substantially regular intervals during such immersion. Each of these additions of hypophosphite may be in the amount, e.g., of about five grams of hypophosphite per liter of the bath.

The following Table I illustrates an example of a plating process embodying the principles of this invention.

Table I

Material	Grams/Liter	Operating Conditions
NiCl ₂ ·6H ₂ O	15	Temperature 93° C. pH 9.1. pH Control NH ₄ OH—Concentrated.
CoCl ₂ ·6H ₂ O	15	
NH ₄ Cl	50	
Na ₂ C ₂ H ₃ O ₇ ·2H ₂ O	100	
NaH ₂ PO ₃ ·H ₂ O	10	

In the example of the foregoing Table I varying quantities of the cobalt and nickel salts may be provided as long as the total salt concentration is maintained at 30 grams per liter.

The following Table II illustrates the results achieved in plating baths embodying the electroless process of this invention.

Table II

Example	Plate Time (minutes)	Electro-Cycle (sec./min.)	Film Thickness (inches)	Total Current (amps.)	Current Density (amps./ft. ²)	pH	Potential (volts)
1	60	0	.0003	0	0	9.5	0
2	60	0	.0003	0	0	9.5	0
3	60	0	.0003	0	0	9.5	0
4	90	10	.001+	4.0	12.1	9.2	1.5
5	30	10	.0003	4.0	12.1	9.2	1.5
6	30	10	.0003	2.0	6.0	9.2	1.5
7	30	10	.0003	2.0	6.0	8.5	1.5
8	30	10	.0003	1.0	3.0	8.2	1.0
9	30	10	.0003	1.0	3.0	8.2	1.0
10	25	10	.0003	0.3	1.0	9.0	1.0
11	30	10	.0003	1.0	3.0	9.3	1.0
12	30	10	.0003	1.5	4.5	9.7	1.5
13	80	10	.0005	1.5	4.5	9.5	1.2

each successive unit interval of time in the electroless process.

The addition of a small direct current in intervals of a few seconds increases the deposition rate of the electroless process. The electric current provides an electrochemical action on the bath which acts as a catalyst causing gassing on the cathode with the result that more hydrogen ions necessary to the electroless process are released from the cathode. The cathode is thereby cleaned which effects a restart of the electroless chemical process. In this manner, an electric current serves as a catalyst to restart the chemical process and restore the electroless process to its original rate. It is to be realized that the addition of a small current density direct current at periodic intervals does not increase the rate of deposition by reason of an electroplating action. The electric current acts as an aid to the chemical reduction process, and in effect, increases the rate of deposition of the electroless process. In effect then, the addition of an electric current to the bath provides an improved electroless process.

The cyclic application of direct current to the bath has the effect that an occasional small lowering of the phosphorus content of the deposit results from the addition of the current. This is to be expected because the presence of any value of electric current in the electroless bath will deposit essentially phosphorus free nickel. Therefore, for a given volume of material to be plated a smaller percentage will be a nickel phosphorus alloy and a larger percentage will be pure electrolytically deposited nickel. This effect may be compensated for by the adjustment of the phosphite ion concentration within the bath. To maintain the hypophosphite ion concentration in the bath at about the desired level throughout the period when the metallic objects to be plated are immersed therein, additional hypophosphite may be added to the

As can be seen from the foregoing Table II, in Examples 1 to 3, representing a pure electroless process, the film thickness achieved for a plating time of 60 minutes was .0003 inch. This same thickness was achieved by the process of the invention, typically illustrated by Example 10, in 25 minutes with the addition of a D.C. pulse current.

The bath compositions of the foregoing examples are useful in plating objects of any of the metals heretofore described.

The soluble nickel salts serve as a source of the nickel ions and the nickel plating in the hypophosphite serves as the reducing agent. The organic salts and the ammonium salts have to hold the nickel salts in solution. The preferred organic salt is sodium citrate, the ammonium chloride serves to maintain the bath alkalinity and also to hold the nickel salts in solution.

The aforescribed electroless process is particularly advantageous in the plating of metals such as to be used in the automotive industry wherein there is desired a uniform and corrosion resistive finish of high durability. The addition of the direct current to the electroless process provides an even rate which allows for a thick enough deposit of nickel on the metal finish to meet the desired specifications.

Although the invention has been described and illustrated in detail, it is to be clearly understood that the same is by way of illustration and example only and is not taken by way of limitation, the spirit and scope of this invention being limited only by the terms of the appended claims.

We claim:

1. In the process for depositing a nickel-containing coating onto a surface of a metallic object, which process comprises applying an aqueous solution containing nickel

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ions and hypophosphite ions to said surface for a time sufficient to permit deposition of nickel onto said surface by the reduction thereof of some of said nickel ions of said solution by some of said hypophosphite ions thereof, the improvement comprising

supplying a succession of pulses of unidirectional current through said applied solution to said surface of said metallic object, said metallic object being poled cathodically during each of said current pulses, the current density at said surface during each of said current pulses being between about 0.1 ampere per square foot and about 10 amperes per square foot, the duration of each of said current pulses being between about one second and about ten seconds, and the interval between the inception of successive ones of said pulses being about one minute, and

continuing said application of said solution and said supplying of said current pulses for a time greater than that required for two successive ones of said pulses to be supplied to said surface.

2. An improved process according to claim 1, wherein said solution is maintained between about 92 degrees centigrade and about 95 degrees centigrade during said application of said solution to said surface.

3. An improved process according to claim 1, wherein the pH of said solution is maintained between about 8.2 and about 10 during said application of said solution to said surface.

4. An improved process according to claim 1, wherein during said application of said solution to said surface, the pH of said solution is maintained between about 8.2 and about 10 and the temperature of said solution is maintained between about 92 degrees centigrade and about 95 degrees centigrade.

5. An improved process according to claim 4, wherein said metallic object contains at least one metal selected from the group consisting of iron, copper, nickel, cobalt, copper and copper-base alloys, said nickel ions are supplied by a nickel salt dissolved in said solution in a maximum concentration of about three percent-by-weight, said hypophosphite ions are supplied by an alkali-metal hypophosphite salt dissolved in said solution in a max-

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imum concentration of about one percent-by-weight, and said solution additionally contains at least one salt selected from the class consisting of sodium citrate and ammonium chloride in a concentration such as to maintain said pH of said solution between about 8.2 and about 10.

6. An improved process according to claim 1, wherein said solution additionally comprises cobalt ions, ammonium chloride and sodium citrate and said coating deposited therefrom contains both cobalt and nickel.

7. An improved process according to claim 1, wherein said metallic object contains at least one metal selected from the group consisting of steel, iron, cobalt, nickel, copper and copper-base alloys, each liter of said solution initially consists essentially of the following compounds in about the following masses:

	Grams
Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	A
Cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$)	B
Ammonium chloride (NH_4Cl)	50
Sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$)	100
Sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$)	10
Water (H_2O) to make one liter of said solution.	

the sum of said A grams and said B grams being about 30 grams, and

during said application of said solution to said surface, the pH of said solution is maintained between about 9.0 and about 9.2 by addition thereto of ammonium hydroxide and the temperature of said solution is maintained between about 93 degrees centigrade and 95 degrees centigrade.

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JOHN H. MACK, *Primary Examiner*.

JOHN R. SPECK, *Examiner*.

G. E. BATTIST, G. KAPLAN, *Assistant Examiners*.