United States Patent Office 2,721,814 Patented Oct. 25, 1955

2,721,814

NICKEL PLATING BY CHEMICAL REDUCTION

Hillard J. Jendrzynski and Thomas F. Stapleton, Detroit, Mich., assignors to General Motors Corporation, Detroit, Mich., a corporation of Delaware

No Drawing. Application January 26, 1954, Serial No. 406,353

4 Claims. (Cl. 117—130)

This invention relates to the deposition of metals by chemical reduction and more particularly to improvements in the deposition of nickel from chemical reduction plating solutions.

It is known that nickel may be deposited in a substantially pure condition upon a catalytic article immersed in an aqueous solution of a nickel salt, a reducing agent and certain additives. The plating reaction may be expressed as follows:

$$Ni^{++} + H_2PO_2^- + H_2O \xrightarrow[\text{heat}]{\text{catalyst}} Ni^0 + H_2PO_3^- + 2H^+$$

The kinetics of this reaction may be expressed as in terms of adsorption as:

$$Ni^{++}\text{ (in solution)} \rightleftarrows Ni^{++}\text{ (adsorbed and activated)} \rightleftarrows Ni^0\text{ (reduced)}$$

Such a chemical reduction deposition of nickel has several advantages over conventional nickel electroplating methods. For example, chemical reduction plating provides a deposit of substantially uniform thickness over even the most irregularly shaped articles, the deposited nickel being characterized by good adherence and strength. Hence, it is a process which has a potentially widespread use in industrial applications. However, up to the present time, chemical reduction plating methods have not achieved widespread use because of their relatively high cost and the high degree of solution control heretofore required.

In prior chemical reduction plating processes difficulties have been encountered by the accumulation in the plating bath of undesirable products of the oxidation-reduction plating reaction. As a result, it has generally been necessary either to attempt expensive bath purification treatments or to limit the use of chemical reduction plating to specialized applications where the unique characteristics of a chemical reduction nickel coating are desired regardless of cost.

We have now discovered that the aforementioned difficulties can be avoided by the practice of the present invention as hereinafter described.

We have discovered that, contrary to prior ideas concerning chemical reduction plating, superior results are obtained employing a bath containing only ions of the metal to be deposited, a buffer and a reducing agent, hence, in the case of nickel plating, nickel ions and preferably a hypophosphite reducing agent.

Those metals and alloys which have been found to exert catalytic effects on the oxidation-reduction plating reaction and hence may be coated with nickel by the practice of the present invention include steel, iron, platinum, silver, nickel, gold, cobalt, palladium and aluminum. It will be understood, of course, that for a superior quality nickel deposit the surface of the article to be coated should be thoroughly cleaned. Accordingly, in many instances it is desirable to employ conventional plating pretreatment, such as buffing, abrading or acid etching, prior to chemical reduction plating.

In the practice of our invention the aforementioned difficulties are avoided and an improved metallic deposit is obtained by immersing a catalytic article into a relatively dilute aqueous solution consisting essentially of nickel ion, a buffer, preferably an acetate, and hypophosphite reducing agent. The reduction plating is then continued until the nickel ion content is substantially exhausted as indicated by the disappearance of the green color in solution caused by the presence of nickel ions. By such a process not only is an improved deposit obtained, but also the process may be operated at a lower temperature than heretofore thought feasible. For example, we have obtained excellent results operating at a temperature of about 165° F. to 190° F.

The practice of the present invention permits widespread use of chemical reduction plating processes by eliminating unnecessary bath ingredients and so formulating the bath's active ingredient content to provide that the nickel content will be substantially completely deposited from solution in a given time, as for example, during an eight hour shift or a four hour period, at which time the plating solution is discarded. Since the plating process is allowed to continue to completion, no pH control or maintenance is necessary after initially establishing a pH preferably within the range from about 6.0 to 6.2.

The nickel ion is provided by a water-soluble nickel salt, for example, as nickel acetate, nickel chloride, etc. The reducing agent preferably is the hypophosphite radical which may be introduced as an alkali metal hypophosphite such as sodium hypophosphite, an alkaline earth hypophosphite, ammonium hypophosphite, or as hypophosphorous acid.

A chemical reduction plating solution in accordance with the present invention is formed by adding a soluble nickel salt to water in an amount necessary to deposit a desired thickness of nickel on a particular surface. This amount, of course, can be calculated for a particular article. The hypophosphite reducing agent is then added to the solution, the quantity being determined by the amount of nickel to be reduced. Generally it is advisable to provide an additional amount of hypophosphite radical to accommodate side reactions and to promote the plating reaction during the final reduction stages. We have found that excellent results are obtained when an additional amount of hypophosphite is provided, over and above that required to completely reduce the nickel, in an amount approximately to 100 to 300% of that required to completely reduce the nickel added.

When a source of nickel other than nickel acetate is employed, to maintain the pH value of the plating solution just below the point at which the solution is saturated with nickel phosphite, it is at times desirable to utilize as a buffer a small amount of acetate radical, added as an acetic acid and/or an alkali metal acetate such as sodium acetate, an alkaline earth acetate or ammonium acetate, the optimum ratio of acetate to nickel in solution being about 2 to 3.

The following are illustrative examples of initial plating bath compositions and conditions in accordance with the present invention wherein the quantities are expressed in terms of grams per liter:

Example I

$Ni(C_2H_3O_2)_2 \cdot 4H_2O$	16.7
$NaH_2PO_2 \cdot H_2O$	20.0
Temperature	182
pH (initial)	6.8
Work load ($cm.^2/cm.^3$)	0.06
Reduction completed, hr.	4
Average plating rate, $mg./cm.^2/hr.$	10.5

Example II

$Ni(C_2H_3O_2)_2 \cdot 4H_2O$	11.1
$HC_2H_3O_2$	2.2
$NaH_2PO_2 \cdot H_2O$	13.3
Temperature	182
pH (initial)	6.0
Work load ($cm.^2/cm.^3$)	0.06
Reduction completed, hr	3
Average plating rate, $mg./cm.^2/hr$	8.2

Example III

$NiCl_2 \cdot 6H_2O$	16.7
$HC_2H_3O_2$	11.1
$NaH_2PO_2 \cdot H_2O$	20.0
Temperature	171
pH (initial)	6.5
Work load ($cm.^2/cm.^3$)	0.06
Reduction completed, hr	4.5
Average plating rate, $mg./cm.^2/hr$	8.8

Example IV

$Ni(C_2H_3O_2)_2 \cdot 4H_2O$	16.7
$NaH_2PO_2 \cdot H_2O$	20.0
Temperature	171
pH (initial)	6.5
Work load ($cm.^2/cm.^3$)	0.06
Reduction completed, hr	4.5
Average plating rate, $mg./cm.^2/hr$	8.0

Example V

$Ni(C_2H_3O_2)_2 \cdot 4H_2O$	5.5
$HC_2H_3O_2$	1.1
$NaH_2PO_2 \cdot H_2O$	6.6
Temperature	182
pH (initial)	6.5
Work load ($cm.^2/cm.^3$)	0.06
Reduction completed, hr	2.5
Average plating rate, $mg./cm.^2/hr$	5.4

Example VI

$Ni(C_2H_3O_2)_2 \cdot 4H_2O$	16.7
$HC_2H_3O_2$	3.3
$NaH_2PO_2 \cdot H_2O$	20.0
Temperature	164
pH (initial)	5.8
Work load ($cm.^2/cm.^3$)	0.06
Reduction completed, hr	5.5
Average plating rate, $mg./cm.^2/hr$	7.7

While the amount of nickel ion to be employed obviously can be varied somewhat without going beyond the scope of this invention, we have found that it is essential to utilize an initial nickel ion concentration not substantially in excess of about 10 grams per liter. Similarly, we have found that when a hypophosphite radical is utilized as a reducing agent, superior results are obtained when its concentration does not exceed about 25 grams per liter. In those instances where it is desired to use an acetate or other buffer, the amount should not exceed about 15 grams per liter with an amount within the range from about 1 to 3.5 grams per liter initial concentration being preferred.

From the foregoing description of the invention it will now be understood that we have provided an improved method of chemical reduction plating in which the operating temperature is substantially reduced, the necessity for adding bath makeup constituents being eliminated and an improved metallic deposit is obtained.

It is to be understood that, although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited since changes and alterations therein may be made which are within the full intended scope of this invention as defined by the appended claims.

What is claimed is:

1. A method of depositing nickel from a chemical reduction plating bath, said method comprising immersing a catalytic article to be coated in a solution of nickel ion and a hypophosphite reducing agent capable of reducing the nickel in solution, said solution having a nickel ion concentration of less than about 10 grams per liter, a hypophosphite ion concentration of less than about 25 grams per liter, a temperature within the range from about 165° F. to 190° F. and an initial pH within the range from about 5.8 to 7.2, and allowing said article to remain in said solution until the nickel is substantially completely reduced as evidenced by the solution turning from green to colorless.

2. A method of depositing substantially pure nickel on a catalytic surface by chemical reduction plating, said method comprising immersing the article to be coated in an aqueous solution of nickel acetate and sodium hypophosphite, the nickel ion concentration of said solution being less than about 10 grams per liter and the hypophosphite ion concentration being less than about 25 grams per liter, said solution having an initial pH within the range of about 5.8 to 7.2 and being maintained at a temperature within the range from about 165° F. to 190° F., and maintaining said article in such solution for a time sufficient to reduce substantially all of the nickel in solution as evidenced by the solution turning from green to colorless.

3. A method of depositing nickel from a chemical reduction plating solution which comprises immersing the articles to be plated in an aqueous solution containing nickel ion, acetate ion and hypophosphite ion, and having an initial pH from about 5.8 to 7.2, the nickel ion concentration being less than about 10 grams per liter, the hypophosphite ion concentration being less than about 25 grams per liter and the ratio of acetate ion to nickel ion being within the range from 2 to 1 to 3 to 1, maintaining said solution at a temperature within a range from 165° F. to 190° F., and allowing said articles to remain in said solution for a time sufficient to reduce substantially all the nickel in the solution.

4. A method of depositing nickel from a chemical reduction plating solution which comprises immersing the articles to be plated in an aqueous solution of nickel chloride, an alkali metal hypophosphite and a soluble acetate, and having an initial pH from about 5.8 to 7.2, the nickel ion concentration being less than about 10 grams per liter, the hypophosphite ion concentration being less than about 25 grams per liter and the ratio of acetate ion to nickel ion being within the range from 2 to 1 to 3 to 1, maintaining said solution at a temperature within a range from 165° F. to 190° F., and allowing said articles to remain in said solution for a time sufficient to reduce substantially all the nickel in the solution.

References Cited in the file of this patent

UNITED STATES PATENTS

2,658,841 Gutzeit et al. ---------- Nov. 10, 1953