CHEMICAL NICKEL PLATING


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9 Claims

ABSTRACT OF THE DISCLOSURE

In electroless nickel plating baths, plating rate stabilizers selected from the group consisting of 1,3-diisopropylthiourea and thiobenzanilide.

This invention relates to nickel plating and, more particularly, to the chemical deposition of nickel from an aqueous solution containing a soluble nickel salt and a suitable reducing agent, such as a hypophosphite compound.

Basically, such deposition involves the reduction of nickel ion to nickel metal by the hypophosphite ion, or probably by the reaction product of the hypophosphite ion with water. The deposition is catalyzed at least initially by the metal of the workpiece and thereafter autocatalyzed by the nickel metal which is plated. The deposition reaction is represented by the equation:

\[ \text{Ni}^{2+} + 2\text{H}_{2}\text{PO}_{2}^{-} + 2\text{H}_{2} \xrightarrow{\Delta} \text{Ni} + 2\text{H}_{2}\text{PO}_{2}^{-} + 2\text{H}^{+} \]

Electroless nickel plating has found a number of useful applications and it has certain advantages over other methods of plating, such as electrodeposition, chiefly because it provides an extremely uniform plating thickness regardless of the shape of the workpiece; thus uniform, dense, nonporous plate of high quality can be attained on workpieces of highly complex contour. Some of the disadvantages of the electroless nickel plating process have been the relatively slow rate of deposition and the tendency for the bath to decompose. The first of these problems has been solved, to some extent, by the addition of less than 0.0005 g./l. of certain thiocompounds, such as thiourea, or potassium thiocyanate, which increase the plating rates of the baths. The second of these disadvantages has also been solved, to some extent, by the addition of less than 0.2 g./l. of thiocompounds such as thiourea among others. Hence, certain thiocompounds in certain concentrations have been used in electroless nickel baths by the prior art for one or the other reason. However, the particular thiocompounds used heretofore and the concentrations employed have not solved another major problem that still exists with these baths. That problem is the stability of the plating rate. By plating rate stability, we mean that property of the bath which permits it to deposit nickel at substantially the same rate over a given period of time, preferably at least 4 hours or the equivalent of half a work shift. Baths which plate at substantially the same rate over a reasonable period of time before needing to be discarded obviously lend themselves more readily to production applications than those which have variable or decreasing plating rates. Such variable/decreasing plating rate baths, which are typical of the prior art, need frequent changing amounting to a considerable amount of production down-time.

It is, therefore, an object of our invention to both increase and stabilize the plating rates of electroless nickel baths.

FIGURE 1 is a graphical representation of the performance of baths within the scope of our invention.

FIGURE 2 is a graphical representation of the performance of baths other than those of our invention.

Briefly stated, our invention comprises the addition of a compound from the group consisting of thiobenzenilide and 1,3-diisopropylthiourea to an electroless nickel bath to both increase and stabilize the plating rate of the bath over a fixed period of time. More specifically, our invention comprises the addition of small, but effective, amounts but less than 0.047 g./l. of the former and less than 0.009 g./l. of the latter.

Though the additives of our invention may be used in conjunction with any hypophosphite type electroless nickel deposition bath, I prefer to use them in conjunction with a bath and process of the type disclosed and claimed in U.S. Patent 2,876,116 Jedrzejski, filed Dec. 29, 1955, and assigned to the assignee of this invention. The aforesaid patent is directed toward the addition of less than 0.02 g./l. of molybdenum to stabilize electroless nickel deposition baths. In this connection, then, we prefer to use the additives of our invention in conjunction with a bath comprising about 11.8–22.3 g./l. of nickel sulfate hexahydrate, 11.8–22.3 g./l. of sodium hypophosphite monohydrate, 6.71–17.2 g./l. of acetic acid, 0.0088–0.0116 g./l. of molybdenum, and sodium hydroxide to a pH of 5.5. We prefer to add the molybdenum to the solution by adding thereto 0.087–1.14 ml./l. of an 85% molybdic acid solution. Within the range of the bath recited above, optimum results, in terms of plating rate, have been obtained using a solution comprising the 11.8 g./l. of nickel sulfate hexahydrate, 22.3 g./l. of sodium hypophosphite monohydrate, 9.34 ml./l. of acetic acid, 0.88 ml./l. of an 85% molybdic acid solution, and sodium hydroxide to a pH of 5.5. Obviously, as is known in the art, other compounds may be employed in making up the bath to be used in our invention. In this connection, any of the commonly known soluble nickel salts may be employed. These include nickel chloride, nickel sulfate, and nickel acetate. The concentration of the nickel ion should be from 1–15 g./l. The hypophosphite ion may be added in the form of hypophosphoric acid, sodium hypophosphite or other soluble hypophosphites. The hypophosphite ion concentration should be from about 2–40 g./l. pH in the range of 4.5–6.0 may be employed with adjustment thereof by the addition of sodium hydroxide. As is the normal practice, a suitable buffer may be used in order to adjust and maintain the proper pH. The amount of buffer used will, of course, depend upon its molecular weight and the number of effective carboxyl groups per molecule, since from 1.5 to 2.5 effective carboxyl groups per nickel ion will provide effective buffering. When acetic acid hypophosphoric acid is used, from 2–30 g./l. are generally sufficient.

In some instances it may be desirable to also include in the bath a chelating agent such as glycine, glycineol acid, ethylenediaminetetraacetic acid, and the like, particularly where the nickel ion concentration is high. The chelating agent functions to maintain the nickel in solution by forming a soluble complex ion with at least a portion of the nickel. Some compounds, for example glycine, serve not only as a chelating agent, but also as a buffer to maintain the desired pH.

To the above-identified baths among others, is added either 0.003–0.004 g./l. of 1,3-diisopropylthiourea or 0.007–0.012 g./l. of thiobenzanilide concentrations of 0.0008–0.009 g./l. of 1,3-diisopropylthiourea and 0.0001–0.047 g./l. of thiobenzanilide improved the plating rate.
and the plating rate deviation, but the aforesaid narrower concentration ranges produced optimum results. By plating rate deviation, we mean the change in plating rate (i.e., $dY/dX$) that occurs over the 4-hour period when compared to the initial plating rate. By improving the deviation, we minimize the magnitude of this change. 1,3-diisopropylthioureia in the concentrations indicated increased the total deposit 95% over that obtained from the standard solution not containing the additive over the same 4-hour plating time. Thiobenzenilide in the concentrations indicated increased the total deposit 84% over the standard bath not containing the additive over the same 4-hour plating time. The plating rate deviation of the bath containing the 1,3-diisopropylthioureia was less than .15 mil/hr. over a four-hour plating period, which amounts to about a 15% loss in plating rate as opposed to approximately 39% loss of plating rate over the same period displayed by the standard bath without the 1,3-diisopropylthioureia additive. Similarly, the plating rate deviation of the bath containing the thiobenzenilide was less than .18 mil/hr. over a four-hour plating period, which amounts to about an 18.6% loss in plating rate as opposed to approximately 39% loss of plating rate over the same period displayed by the standard bath without the thiobenzenilide additive.

It should be also noted that both the additives of our invention have increased the initial plating rate of the optimized preferred bath from 0.77 mill/hr. to 0.965 mill/hr./liter, which amounts to about a 25% increase in the initial plating rate. Correspondingly, the fourth hour plating rate increase is 75.2% for 1,3-diisopropylthioureia and 67.7% for thiobenzenilide.

The following is a specific example of our invention. A standard solution comprising 11.8 g./l. of nickel sulfate hexahydrate, 22.3 g./l. of sodium hypophosphite monohydrate, 9.34 g./l. of acetic acid, 0.88 mL/l. (0.009 g./l.) of an 85% molybdc acid solution, and sodium hydroxide to pH of 5.5 was prepared. To one 3.8 liter portion of this solution was added 0.012 g./l. of thiobenzenilide. To a second 3.8 liter portion of this solution was added 0.004 g./l. of 1,3-diisopropylthioureia. A third 3.8 liter portion of this solution was used as a standard solution with which to compare the other solutions. Steel panels (2.54 x 4.39 x 0.66 cm.) were plated in these baths. The panels were first prepared for plating by solvent cleaning, cathodic alkaline cleaning (6 volts, 77°C. 30 sec.), rinsing in water, dipping in 3% HSO₃ for 15 sec., rinsing with water, and heating the panels to the temperature of the plating bath immediately prior to immersion therein. This pre-treatment was adequate for the purpose intended and is in no way critical to the effectiveness of the plating step. However, the preheating of the panel prior to its immersion into the plating bath was found to be a desirable step in that better adhesion and an initially higher plating rate was obtainable. A panel was removed and replaced by a fresh panel at the end of each hour. Each panel was weighed before and after plating to determine hourly plating rates. Agitation was maintained by a reciprocating bar moving the panels at a rate of 167.6 cm. per min. Though temperatures in the order of 66°C. to boiling could be used, the baths were maintained at a temperature of 82°C. plus or minus 1°C. The results of these tests are shown in FIGURE 1 wherein curve 1 corresponds to the standard bath. Curves 2 and 3 correspond to the baths having thiobenzanilide and 1,3-diisopropylthioureia additives respectively therein. The deposits produced in all instances were smooth. It was noted that whereas the additive-free solution produced deposits which were sulfur-free and had a phosphorous content of about 3–5%, the deposits produced from the baths having the additives of our invention therein contained about 0.005% sulfur and about 6.7–9.6% phosphorous. It was also noted that for maximum effectiveness with the test bath, the area to be plated should not exceed more than about 24 cm.² per liter of solution. As the area is increased, the plating rate decreases. Similarly, as the area decreases, the plating rate increases. However, we have determined that while not critical, the 24 cm.² per liter area to volume ratio is about the most practical compromise between plating area and plating rate for our purposes.

FIGURE 2 graphically depicts the often erratic results produced by other apparently chemically similar compounds, some of which have been used by the prior art to effect other results. These curves were produced in the same manner as those produced in FIGURE 1. Curve 4 corresponds to the plating rate deviation produced by a 0.00304 g./gal. addition of 2-mercaptobenzothiazole. Curve 5 corresponds to the plating rate deviation produced by a 0.00152 g./gal. addition of thioacetamide. Curve 6 corresponds to the plating rate deviation produced by a 0.0022 g./gal. addition of diphenylthiourea. Curve 7 corresponds to the plating rate deviation produced by a 0.00076 g./gal. addition of thiourea. Curve 8 corresponds to the plating rate deviation produced by a 0.0022 g./l. addition of benzylthiourea.

Though we have disclosed our invention solely in terms of one specific embodiment thereof, we do not intend to be limited thereto, except as defined by the claims which follow.

We claim:

1. In an aqueous electroless nickel plating bath containing nickel ion and hypophosphite ion, the improvement which consists of including in said bath a small, but effective amount of at least one compound selected from the group consisting of 1,3-diisopropylthioureia and thiobenzenilide, to increase and stabilize the plating rate of said bath.

2. The bath as claimed in claim 1 wherein the concentration of said 1,3-diisopropylthioureia is 0.0008–0.0009 g./l. and the concentration of said thiobenzenilide is 0.0001–0.0047 g./l.

3. The bath as claimed in claim 1 wherein the concentration of said 1,3-diisopropylthioureia is 0.0003–0.0004 g./l., and the concentration of said thiobenzenilide is 0.007–0.012 g./l.

4. The bath as claimed in claim 3 wherein said bath comprises a nickel ion concentration of about 1–1.5 g./l., a hypophosphite ion concentration of about 2–40 g./l., at least one buffer selected from the group consisting of acetic and propionic acid and having a concentration of about 2–30 g./l., and a molybdenum concentration of less than about 0.02 g./l.

5. A bath as claimed in claim 4 wherein said bath comprises about 11.8–22.3 g./l. of nickel sulfate hexahydrate, 11.8–22.3 g./l. of sodium hypophosphite monohydrate, 6.71–17.2 g./l. of acetic acid, and 0.0088–0.0116 g./l. of molybdenum, said bath having an initial pH of from 4.5–6.0 and a temperature from about 66°C. to boiling.

6. The bath as claimed in claim 5 wherein said bath comprises about 11.8 g./l. of nickel sulfate hexahydrate, 22.3 g./l. of sodium hypophosphite monohydrate, 9.34 mL/l. of acetic acid, 0.009 g./l. of molybdenum, and wherein the concentration of said 1,3-diisopropylthioureia is 0.004 g./l., and the concentration of said thiobenzenilide is 0.012 g./l., said bath having an initial pH of about 5.5 and a temperature of about 82°C.

7. In an electroless nickel plating process, the step of immersing the articles to be plated in a bath as defined in claim 4.

8. In an electroless nickel plating process, including the step of immersing the articles to be plated in a bath as defined in claim 5.

9. In an electroless nickel plating process, including the step of immersing the articles to be plated in a bath as defined in claim 6.

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