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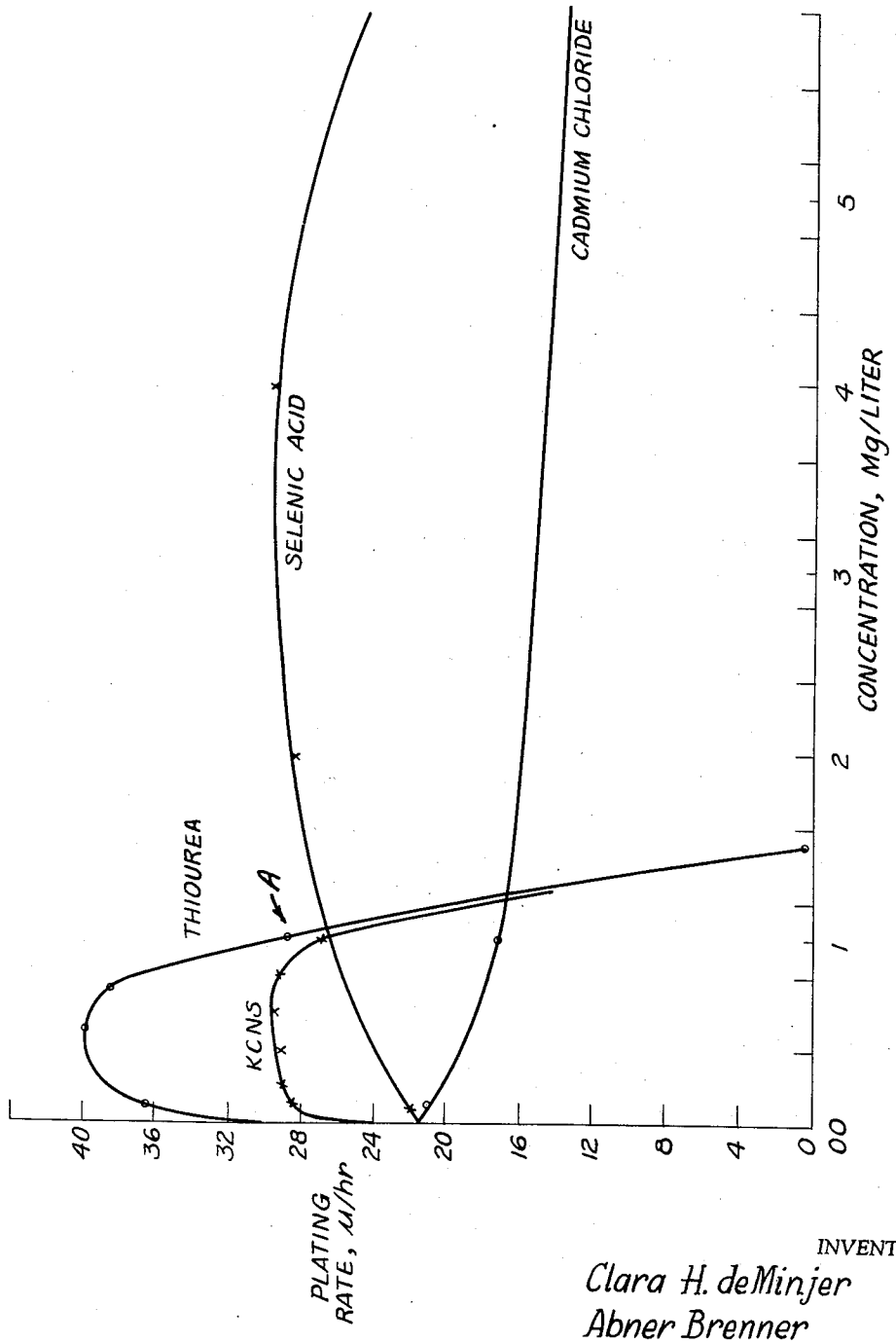

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ELECTROLESS DEPOSITION OF NICKEL

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1 Claim. (Cl. 117—130)

This invention relates to an improvement in the electroless plating of metals and particularly contemplates 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 unique process which produces a sound, adherent, corrosion-resistant coating of a nickel phosphorous alloy without the use of electric current. The coating deposits uniformly over objects of irregular shape and even in the deepest of recesses. Consequently, the process has been finding increasing commercial utilization, because it can accomplish plating operations which are impossible by conventional electrodeposition methods. Details concerning the electroless process can be found in U.S. Patent No. 2,532,283, issued to Brenner and Riddell, and in the following references: NBS Jour. of Research 37, pp. 1–4, 1946; Proc. of the Electroplaters Society 33, 16, 1946; NBS Jour. of Research 39, pp. 385–395, 1947; Proc. of Amer. Elec. 34, pp. 156, 1947; Metal Finishing, November–December 1954.

Due to the commercial adaptation of the plating process described in the above-referred-to patent and publications, it has been found that a faster rate of plating would be desirable. The present rate of deposition is ordinarily about 0.5 mil/hr. and, under certain conditions, can be increased to about 1 mil/hr. It has also been observed that under continuous operation in accordance with the procedural methods described in the references, nickel deposits are gradually formed on the walls of the vessel employed, particularly on scratches or on areas where local overheating occurs. The present invention contemplates an improved plating bath for use in connection with electroless plating, which provides both a substantial increase in the rate of plating obtainable, and which also diminishes the tendency of the bath to deposit nickel on the walls of the container. Ancillary to such objectives, the improvements characterizing the present invention results in an improvement in the brightness of the plated nickel.

It is accordingly an immediate object of the present invention to provide a plating bath and procedure in connection with electroless plating whereby a much greater rate of electrodeposition may be achieved.

Another object of this invention is to provide an improved process and bath which will diminish the tendency for electrodeposition on the walls of the container of the vessel containing the plating bath.

Still another object of this invention is to provide an improved plating bath and method which will result in an enhanced brightness of the plating produced.

Other uses and advantages of the invention will become apparent upon reference to the specification and drawing in which the drawing shows a chart illustrating the effects of various additives on electroless deposition in accordance with the principles of this invention.

In accordance with the principles of this invention, additions are made to the electroless plating bath described in the above-referred-to references which increase the rate of plating, diminish the tendency of the bath to deposit nickel on the walls of the container, and which further aid in the production of a brighter deposit.

The manner in which the above-enumerated improved results are obtained will best be understood by considering briefly the fundamentals of the reaction and certain theoretical ideas. Specifically, the principles underlying the present invention are based upon a theory developed in connection with the electrodeposition of alloys, which theory is singularly applicable to explain electroless deposition.

Briefly reviewing the principal feature of the electroless plating process described in the above references, plating is accomplished by using a bath containing either an ammoniacal or an acid solution of nickel. The basic components include metal salts; hypophosphite ion, which is the active chemical reducing agent; and a complexing agent, such as hydroxyacetate. The complexing agent serves a two-fold purpose: (1) it keeps the metal in the solution in the form of soluble complexes as the pH goes up, and it also serves as a buffer to keep the pH of the bath from changing too rapidly during the plating operation. The basic chemical reaction involved in the process according to the reference patent are as follows:

$$NiCl_2+NaH_2PO_2+H_2O\rightarrow Ni+2HCl+NaH_2PO_3 \quad (1)$$

$$NaH_2PO_2+H_2O\rightarrow NaH_2PO_3+H_2 \quad (2)$$

For the plating of nickel, the metal may be added as a simple salt in a concentration of from 0.05 to 10 parts by weight, a hypophosphite radical of from 0.07 to 7.5 parts by weight and from 50 to 98 parts by weight of water. As fully explained in U.S. Patent No. 2,532,283, the process can be carried out in a pH range varying from 2 to 11; an acid bath being obtained by employing a sodium salt of a weak organic acid such as sodium acetate, sodium citrate or sodium hydroxyacetate and an alkaline bath being accomplished by employing ammonium hydroxide and a salt of a hydroxyl organic acid such as sodium citrate, tartaric acid etc.

Reaction 1 provides the deposition of metal. In this reaction an acid is formed, hence the need of buffers in the solution and the need for adding alkali to the bath as it operates. The second enumerated reaction occurs concurrently with the first and represents a waste of reducing power. The deposition of nickel is about 37% efficient, based on the utilization of hypophosphite. This means that, under the most efficient conditions of deposition, about 5 pounds of sodium hypophosphite are required to produce one pound of nickel.

Returning to a consideration of the above-referred-to theory, it is hypothesized that nickel ion is not directly reduced by hypophosphite. Electroless plating involves two steps which occur almost simultaneously: (1) The discharge of hydrogen; (2) induced deposition of nickel. The mechanism of the latter is assumed to be activation of nickel ions by the excess energy of the hydrogen discharge, which activation enables the nickel ions to react with the hypophosphite ions.

Still in accordance with such theory, one equivalent of hydrogen on discharging can bring about the activation of not more than one equivalent of nickel ions, so that the maximum theoretical efficiency of nickel deposition, based on the consumption of hypophosphite, is 50%. Such theory is in accord with the known fact that the efficiency of metal in deposition is never above 40%.

The theory is of particular value in explaining the effect of variables, such as the nature of the metal surface on which deposition is to be made, temperature, and the presence of addition agents on the efficiency and on the rate of electroless plating. The factors which influence the rate of deposition are of primary interest.

According to the theory, if a metallic surface has too high a hydrogen overvoltage, the chemical energy of the hypophosphite reaction may be insufficient to bring about the discharge of hydrogen. Consequently, the above-enumerated step (2), which involves nickel-deposition, would not occur. Conversely, a lowering of the overvoltage on the catalytic metal surface should increase the rate of discharge of hydrogen, but this would not necessarily lead to an increase in the rate of deposition of nickel. If it is assumed that a certain amount of excess energy of hydrogen discharge is necessary in electroless plating to bring about the activation of nickel ions according to such step (2); then if the overvoltage is too low, hydrogen may discharge freely, and yet not result in activation of deposition of nickel. Thus, this discussion of the mechanism of electroless plating indicates that an optimum-hydrogen overvoltage may in fact exist.

To sum up the situation then, too low an overvoltage prevents activation of nickel according to step (2), and conversely too high an overvoltage inhibits step (1) above.

It is interesting to note that the above-explained theory coincides with readily demonstratable phenomena characterizing the electroless plating process. Specifically when a rough surface which has a low hydrogen overvoltage is employed in the electroless plating bath, hydrogen discharge occurs freely, but without nickel deposition. Furthermore, it has been observed that the nickel deposition never occurs without hydrogen discharge. On the other hand, when metals of high hydrogen overvoltage such as cadmium, lead, mercury, zinc, or tin is employed hydrogen does not discharge from the hypophosphite solution. Consequently, electroless nickel cannot be directly plated over such metals as is well known. According to the premise of step (1) in the above theory which involves the energy of hydrogen discharge, it can be logically concluded that: (*a*) Substances which affect hydrogen overvoltage also have an effect on the electroless plating process and that (*b*) substances that normally poison electroless plating probably act through their effect on hydrogen overvoltage.

On the basis of such deductions, the present invention contemplates the addition to the electroless plating bath of various substances which affect hydrogen overvoltage. It was found that such substances which in moderate concentrations tended to act as poisons, have in fact several beneficial effects on the electroless plating process when employed in low concentrations. A general class of substances which affect hydrogen overvoltage are the inhibitors used in the pickling treatment of steel. Small concentrations of certain substances exert a large effect on hydrogen overvoltage. See, for example, an article by J. William Bockris and B. Conway, Trans. of the Faraday Soc., 45, 989 (1949), and an article by Misch and Bernstein, Jour. of Phys. Chem. 55, 1401 (1951). Knowing the effect of hydrogen overvoltage on the electroless plating process in accordance with the theory as explained above and with the further knowledge of the effect of certain substances on hydrogen overvoltage, a number of substances were found which when added to the electroless bath were found to affect the rate of electroless plating even in concentrations of one part per million of solution. As will be indicated, some of these substances increased the rate of deposition and also stabilized the bath against spontaneous decomposition. Other substances affected the brightness of the deposit, in some instances making it brighter, in others making it matt.

In general, the following substances were found to be especially efficacious in connection with the electroless deposition of nickel: (1) Thiourea; (2) potassium thiocyanate; (3) selenic acid, and (4) cadmium chloride. The chart shown in the drawing illustrates the effect of such substances on the rate of electroless plating for different concentrations of the particular additive employed in mg. per liter. Referring to the drawing, it will be noted that thiourea has the most pronounced effect on the rate of deposition. It increases the rate of metal deposition by 50%, bringing the rate of deposition from about 1 mil to 1.5 mils per hour, a rate which compares favorably to that obtainable in conventional electrodeposition. The optimum concentration of thiourea was found to be about 0.7 mg. per liter; that is, slightly less than one part per million parts of bath. At slightly higher concentrations, for example, several milligrams per liter, the poisoning effect of the additive compound is strongly evident as indicated by the region marked A in the drawing.

The addition of thiourea to the electroless plating bath in the optimum concentration indicated in the drawing has another beneficial effect on the operation of the process described in the previously-referred-to references. Specifically, it is effective in preventing the troublesome and hitherto unsolved problem of gradual, spontaneous deposition of nickel on the walls of the containing vessel. The effectiveness of thiourea in such connection is apparently due to adsorption of the additive on the walls of the vessel and on the surface of the object during plating. In addition, it was found that the addition of thiourea also improved the brightness of the deposit.

The effect of potassium thiocyanate and selenic acid on deposition is also indicated in the drawing. As shown, such additives increase the rate of nickel deposition, but not to the extent exhibited by thiourea. The addition of thiocyanate results in a matt deposit while selenic acid improves the brightness of the deposition.

As indicated in the drawing, the effect of cadmium chloride as an additive to the electroless plating bath results in a slight decrease in the rate of plating. However, it is considered beneficial to the process in view of its effect in improving the brightness of the resulting deposit. Specific embodiments of the process according to this invention are illustrated in the following examples.

EXAMPLE I

An acid electroless nickel plating bath is prepared in accordance with the teachings of the above-identified Patent No. 2,532,283. The bath has the following composition:

	G./l.
Nickel chloride, $NiCl_2 \cdot 6H_2O$	30
Sodium hydroxyacetate, $NaC_2H_3O_3$	50
Sodium hypophosphite, $NaH_2PO_2 \cdot H_2O$	10

pH 4 to 4.5.

In accordance with the teachings in the reference patent, the hypophosphite radical in the plating bath may also be secured by the use of ammonium hypophosphite or potassium hypophosphite. To this bath is added thiourea, in an amount of 1 mil per liter of bath. The bath is operated in a temperature range between 95° to 100° C. A steel specimen which has been previously degreased, is cleaned in a conventional manner dipped in hydrochloric acid, rinsed, and immersed in the bath. Deposition of a nickel-phosphorous alloy takes place at a rate of about 30 microns per hour which is about 50% faster than the 20 microns per hour rate which occurs in the absence of a thiourea additive. No deposition of nickel was observed to form on the vessel containing the bath even after long operation of the bath.

EXAMPLE II

An electroless plating bath as in the referred-to patent having the following composition is prepared:

	G./l.
Nickel chloride, $NiCl_2 \cdot 6H_2O$	30
Sodium citrate, $Na_3C_6H_5O_7 \cdot 2H_2O$	15
Sodium acetate, $NaC_2H_3O_2 \cdot 3H_2O$	5
Sodium hypophosphite, $NaH_2PO_2 \cdot H_2O$	10

pH 4 to 4.5.

A selenic acid additive is added in a concentration of 3

milligrams per liter of bath. The operation of the bath to produce deposition and the preparation of the sample is similar to that described in connection with Example I. The rate of deposition of nickel-phosphorus alloy was observed to increase about 50% over the rate of deposition from the bath without the additive. Moreover, the deposits obtained with the selenic acid additive were found to be brighter and of more uniform appearance than those obtained without the additive.

The above-described baths are exemplary and it will be apparent that the additives can also be combined with the various electroless baths specifically enumerated in Patent No. 2,532,283 above-referred-to. The various additives including potassium thiocyanate and cadminum chloride can be interchangeably employed with either of the above-exemplified baths as well as those described in the reference patent.

The influence of the above-referred-to additives when added to an acid electroless nickel bath is further detailed in the following tables.

Table I

mg. additive per liter	microns per hour	appearance
Selenic acid:		
0	21.6	bright.
0.1	22.1	very bright.
1	27.0	Do.
2	28.2	Do.
4	29.6	Do.
6	24.8	Do.
10	13.2	bright, pits.
20	0	no deposit.
Thiourea:		
0	21.6	bright.
0.01	19.4	Do.
0.1	36.6	very bright.
0.5	39.9	Do.
0.75	38.7	Do.
1.0	29.0	Do.
1.5	0.6	very thin.
2	0	no deposit.
Potassium thiocyanate:		
0	21.6	bright.
0.1	28.8	matt.
0.2	29.1	Do.
1	27.2	Do.
2	0.2	no deposit.
10	0	Do.
Cadmium chloride:		
0	21.6	bright.
0.1	21.1	Do.
1	17.2	very bright.
10	11.5	bright, streaks.
100	0.9	stained.

Table II

Additive	Rate of deposition	brightness	stability
Selenic acid	Increases to a maximum.	Improved	No influence.
Thiourea	do	do	Improved.
Potassium thiocyanate	do	Matt	No influence.
Cadmium chloride	Decreases	Improved	Do.

What is claimed is:

In an autocatalytic chemical reduction process for continuously plating nickel on metallic objects, a plating bath comprising an aqueous solution of a nickel salt, the nickel ion being present in an amount not substantially in excess of about 1 part by weight to about 100 parts by weight of said solution, an alkaline hypophosphite, the hypophosphite radical being present in an amount not substantially in excess of about 1 part by weight to about 100 parts by weight of said solution, sodium hydroxyacetate in an amount not substantially in excess of about 5 parts by weight to about 100 parts by weight of said solution, and an additive for increasing the rate of deposition of electroless nickel, said additive consisting essentially of selenic acid in a concentration range of from 0.1 part per 1,000,000 parts to 10 parts per 1,000,000 parts of said solution.

References Cited in the file of this patent

UNITED STATES PATENTS

2,762,723 Talmey et al. ---------- Sept. 11, 1956