Nov. 24, 1964 J. S. SALLO ETAL 3,158,500

PROCESS FOR ELECTROLESS DEPOSITION

Filed Feb. 12, 1962 2 Sheets-Sheet 1

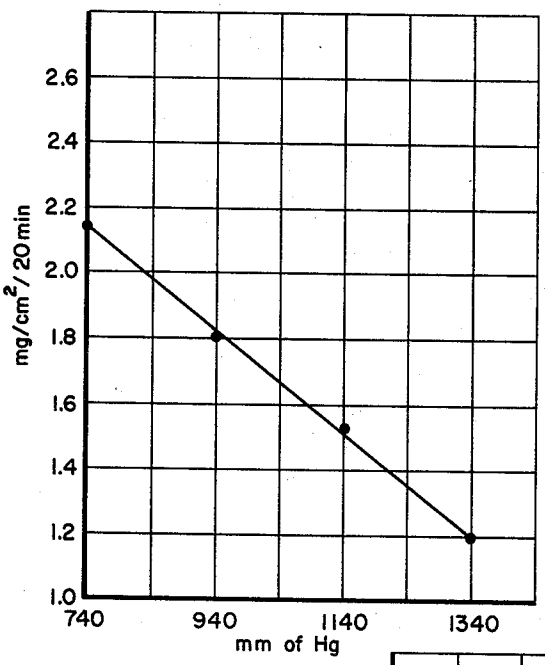


Fig 1

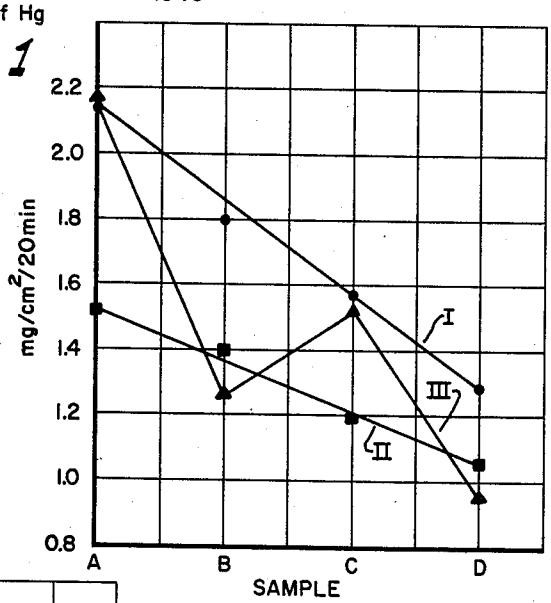


Fig 2

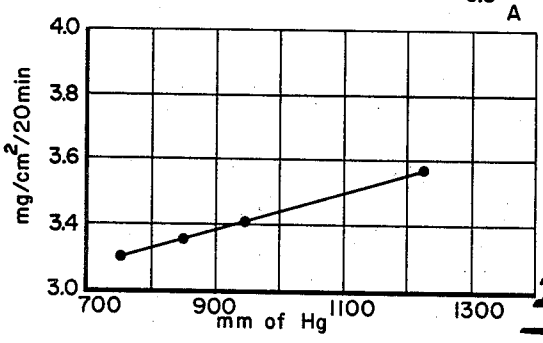


Fig 3

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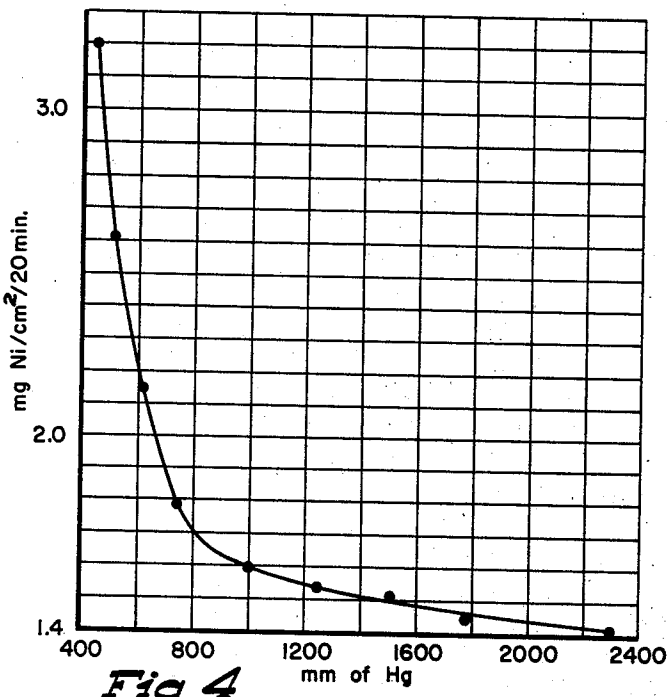


Fig 4

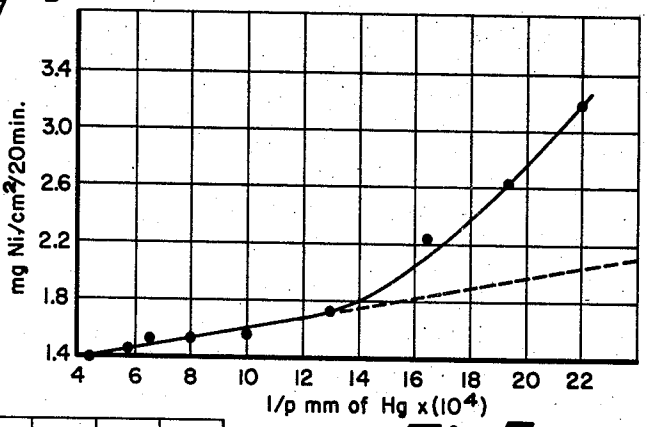


Fig 5

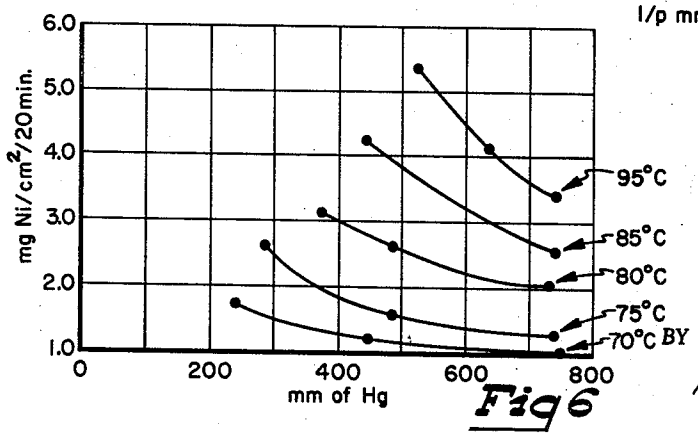


Fig 6

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PROCESS FOR ELECTROLESS DEPOSITION

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This invention relates broadly to processes for chemical nickel plating and improvements therein. More specifically, this invention relates to an improved process for obtaining increased rate of nickel deposition in chemical baths. Experimentally, reduced pressures (essentially below atmospheric) have been found to increase the deposition rate of nickel in certain types of chemical baths, and increased pressures (above atmospheric) have been found to increase the deposition rate of nickel in other specific types of chemical baths.

Chemical nickel plating can occur from two distinctly different types of baths. One such type of bath was developed by Abner Brenner and Grace Riddell at the Bureau of Standards and is claimed in United States Patent 2,532,283. This type of bath will herein be referred to as the Brenner-Riddell bath. A second type of bath is that claimed in two patents to Gutzeit et al., United States Patents 2,658,841 and 2,658,842, herein referred to as the Gutzeit-Krieg bath.

The Brenner-Riddell bath has experimentally been found to be transport controlled. Transport controlled systems are also known as diffusion controlled systems. In such systems, the deposition rate is not dependent on the concentration of the constituents present but is dependent on the ability of one of the constituents to escape or enter the reactive system. It has also been determined that the rate of deposition in a transport controlled bath increases with decreased pressures.

The Gutzeit-Krieg bath has been found to be non-transport controlled and thus the rate does not respond to decreased pressures (below atmospheric). To the contrary, the rate of deposition in this type bath has been found to increase with increased pressures.

Accordingly, it is an object of the present invention to provide an increase in the rate of deposition of the Brenner-Riddell bath by means of reduced pressures.

It is a still further object of the present invention to provide an increase in the deposition rate of a chemical plating bath of the Gutzeit-Krieg type by an increase in pressure.

These and other objects and advantages will become apparent in the following specification taken together with the accompanying drawings wherein:

FIGURE 1 shows the effect of increased pressure (above atmospheric) upon the rate of nickel deposition in a Brenner-Riddell type bath.

FIGURE 2 shows the effect of pressure on the plating of:

(1) A series of four 20-minute samples from a bath of the Brenner-Riddell type at atmospheric pressure (curve I).

(2) A series of four 20-minute samples at 1140 mm. of Hg from a Brenner-Riddell type bath (curve II).

(3) Series of four 20-minute samples from a Brenner-Riddell type bath, samples A and C at atmospheric pressure, samples B and D at 1140 mm. of Hg (curve III).

FIGURE 3 shows the effect of increased pressure upon the rate of nickel deposition from a Gutzeit-Krieg type bath.

FIGURE 4 shows the unexpected and extremely rapid increase in rate of nickel deposition obtained with reduced pressures (below atmospheric) in a Brenner-Riddell type system (transport controlled system).

FIGURE 5 shows the inverse pressure dependence of the rate of nickel deposition in a Brenner-Riddell type system.

FIGURE 6 shows the effect of temperature on the rate of nickel deposition at various reduced pressures for the Brenner-Riddel type bath.

The Brenner-Riddell process teaches that coatings of nickel may be deposited by the chemical reduction of nickel from an aqueous bath containing hypophosphite ions. Such a bath generally consists of nickel ion and hypophosphite ion in the range of 3 to 100 parts by weight with the bath being maintained at a temperature of about 70–90° C. and a pH of about 3–7 in order to accomplish deposition. The following is an example of the composition of the bath for nickel deposition which was utilized in obtaining the data and curves presented in this specification.

$NiCl_2.6H_2O$	g./liter	30
$NaH_2PO_2.H_2O$	do	10
Sodium acetate	do	3
Temperature	° C	85

The pH is controlled at 3–7 by addition of buffering agents.

Employing this bath, the deposition of nickel upon the surface of steel can be accomplished but the rate of deposition is very slow.

While the Brenner-Riddell bath offers certain advantages over competing electrolytic processes, it has been found to be uneconomical to produce deposits at such a slow rate. In other words, it is more expensive to carry out than competing electrolytic processes due to the low nickel efficiency of the reaction.

The Gutzeit-Krieg process teaches that an improvement in the rate of deposition can be obtained with a bath containing the same general constituents as that disclosed by Brenner-Riddell. The following is a typical example of the composition of such a bath for nickel deposition.

	G./liter
$NiSO_4.6H_2O$	17
$NaH_2PO_2.H_2O$	24
Sodium acetate	41
Acetic acid	30

The improvement of this process is based on the regulation of the absolute concentration of hypophosphite ion. Gutzeit-Krieg demonstrated that the rate could be increased by regulating the ratio of nickel ion concentration to the hypophosphite ion concentration. The temperature of the bath is maintained near the boiling point and the pH is regulated to the range from about 4 to about 5.6.

Other bath compositions disclosed in the above referenced patents may be used to obtain the improvement of the present invention. Data has been presented for typical compositions of each of these baths for the purpose of clarity.

Since the initial development of the electroless deposition process by Brenner-Riddell and the subsequent improvements proposed by Gutzeit-Krieg, a large amount of data has been published on these systems. Much of the data concerning these baths is conflicting.

Brenner-Riddell report the rate of deposition to be independent of the hypophosphite ion concentration and advance the hypothesis that the efficiency of the reaction varies with the ratio of the area of the catalytic surface to the volume of the solution. Gutzeit-Krieg, utilizing a modified Brenner-Riddell bath, report the reaction to be first order in hypophosphite ion, provided the area of the substrate is small relative to the volume of the solution. It appears that although the two systems are similar in

composition, the mechanisms of these reactions may be different.

The mechanism of rate control in both Gutzeit-Krieg and the Brenner-Riddell process were investigated in an attempt to resolve the conflicting data. It was concluded that a study of the reactions under pressure would be of value in this respect. Consequently, a series of experiments was carried out on both types of baths with varying pressures (above and below atmospheric). All experiments performed at greater than atmospheric pressure in Brenner-Riddell baths showed a decrease in the rate of nickel deposition. The composition of the atmosphere above the bath did not affect the results. FIGURE 1 shows plots of mg. Ni/cm.^{2} of catalytic surface deposited in 20 minutes from fresh baths versus applied pressure. The decrease in rate with applied pressure is apparent. FIGURE 2 shows the results of a series of runs made from single baths for individual samples A, B, C, and D. Curve I shows a normal sequence of four 20-minute samples at atmospheric pressure. The decrease in rate is due to normal bath deterioration. Curve II is an identical curve for a system in which all samples were prepared at 1140 mm. of Hg. Curve II falls off more slowly than does curve I because bath deterioration is slower when the system is under pressure. Curve III is for a system in which samples A and C were prepared at 740 mm. Hg while samples B and D were made at 1140 mm. Hg. Curve II point C is lower than curve II point B because of the decreased depletion during prior plating under pressure.

Experiments with pressure in the case of the Gutzeit-Krieg baths showed an increase in the rate of deposition with applied pressure. This system showed none of the effects observed for the Brenner-Riddell type of bath. The results are shown in FIGURE 3. Based on these results, it appears that the mechanism of the reactions in the two baths is different.

A series of experiments was conducted below and above atmospheric pressure on the Brenner-Riddell bath to determine the effect of decreased pressures. The series conducted below atmospheric pressure gave completely unexpected results in that the deposition rate increased very rapidly with a slight decrease in pressure (temperature maintained at 85° C.) The results are shown in FIGURE 4 which is a plot of the deposition rate of nickel versus pressure. It can easily be seen that below atmospheric pressure the rate of nickel deposition increases rapidly in proportion to the decreased pressure. This can be shown more clearly with reference to FIGURE 5 which shows the inverse pressure dependence of the bath. The inverse pressure dependence of the rate of nickel deposition predicts a very steep increase in rate as the pressure is decreased. FIGURE 4 shows the entire range studied and confirms this idea. The rate increase below atmospheric pressure as shown in FIGURE 5 is even greater than predicted. This is probably due to extra agitation caused by boiling of the solution at pressures below atmospheric.

To achieve the maximum deposition rate accomplished by the utilization of reduced pressure in the Brenner-Riddell system, as taught by the present invention, it was determined that it was necessary to examine the effect of reduced pressures in relationship to lowering the boiling point of the bath. A series of further experiments was conducted to determine the optimum conditions which would achieve this result. These experiments were conducted below atmospheric pressure at various temperatures. The results are shown in FIGURE 6.

As is well known, decreasing pressure reduces the boiling point of a liquid. In the method of the present invention, the useable reduced pressure is limited to that where the liquid begins to boil. FIGURE 6 shows that the optimum pressure and temperature at which the maximum rate of nickel deposition takes place is approximately 540 mm. of Hg and 90° C. This figure also shows that the lowest limit for a practical rate increase in deposition is approximately 70° C. and 235 mm. of Hg. These are the practical limits for the Brenner-Riddell system as improved by the present invention.

The results discussed above form the basis of the present invention which can be described as follows. If the system employed for electroless deposition is diffusion or transport controlled, reduced pressure will greatly increase the rate of deposition. A particular system is transport controlled if the rate of deposition is not controlled by the concentration of the constituents present. This condition particularly includes Brenner-Riddell systems and excludes Gutzeit-Kreig systems. Consequently, this invention is a basic improvement of importance in the rate control of Brenner-Riddell systems and the like.

If the system employed for electroless deposition is dependent on the concentration of the constituents present as is the Gutzeit-Krieg system, increased hydrostatic pressures will increase the rate of deposition. Consequently, this invention is also a basic improvement in the rate control of Gutzeit-Krieg systems and the like.

It will of course be recognized that the same limitations apply to plating in the present invention as generally apply to other electroless plating systems. That is, the plating will occur on certain catalytic metals, well known in the art, or upon specially prepared non-catalytic surfaces.

We claim as our invention:

1. An improved process for the electroless plating of nickel from a transport controlled system comprising the steps of: providing an aqueous solution maintained at a pH value in the range of about 3 to about 7, said solution being composed essentially of a soluble nickel salt and a soluble hypophosphite salt; immersing a suitable substrate material in said solution; maintaining said solution within a temperature range from about 70° C. to about 90° C.; decreasing the pressure on said solution to a value below the ambient atmospheric pressure and above the vapor pressure of said solution; and plating said substrate material by auto-catalytic reaction of said nickel salt and said hypophosphite salt.

2. An improved process for the electroless plating of nickel from a transport controlled system comprising the steps of: providing an aqueous solution maintained at a pH value in the range of about 3 to about 7, said solution being composed essentially of a nickel salt and sodium hypophosphite; immersing a suitable substrate material in said solution; maintaining said solution within a temperature range from about 70° C. to about 90° C.; decreasing the pressure on said solution to a value below the ambient atmospheric pressure and above the vapor pressure of said solution; and plating said substrate material by auto-catalytic reaction of said nickel salt and said hypophosphite salt.

3. An improved process for the electroless plating of nickel from a transport controlled system comprising the steps of: providing an aqueous solution maintained at a pH value in the range of about 3 to about 7, said solution being composed essentially of a nickel salt, sodium hypophosphite and sodium hydroxyacetate; immersing a suitable substrate material in said solution; maintaining said solution within a temperature range from about 70° C. to about 90° C.; decreasing the pressure on said solution to a value below the ambient atmospheric pressure and above the vapor pressure of said solution; and plating said substrate material by auto-catalytic reaction of said nickel salt and said hypophosphite salt.

4. An improved process for the electroless plating of nickel from a non-transport controlled system comprising the steps of: providing an aqueous solution maintained at a pH value in the range of about 4 to about 5.6, said solution being composed essentially of a soluble nickel salt and a soluble hypophosphite salt; maintaining the absolute concentration expressed in mole/liter of said hypophosphite within the range from about 0.15 to about 1.20; maintaining the ratio between said nickel and said

hypophosphite within the range from about 0.25 to about 1.60, said range being expressed in molar concentration; immersing a suitable substrate material in said solution; applying pressure above the ambient pressure thereon and plating said substrate by auto-catalytic reaction of said nickel salt and said hypophosphite salt.

5. An improved process for the electroless plating of nickel from a non-transport controlled system comprising the steps of: providing an aqueous solution maintained at a pH value in the range of about 4 to about 5.6, said solution being composed essentially of nickel ions, hypophosphite ions, alkaline ions and acetate ions; maintaining the absolute concentration expressed in mole/liter of said hypophosphite within the range from about 0.15 to about 1.20; maintaining the ratio between said nickel and said hypophosphite within the range from about 0.25 to about 1.60, said range being expressed in molar concentration; immersing a suitable substrate material in said solution; applying pressure above the ambient pressure thereon and plating said substrate by auto-catalytic reaction of said nickel salt and said hypophosphite salt.

6. An improved process for the electroless plating of nickel from a transport controlled system comprising the steps of: providing an aqueous solution maintained at a pH value in the range from about 3 up to about 7, said solution including a nickel salt and an alkaline hypophosphite, the nickel ion being present in an amount not substantially in excess of about 3 parts by weight to about 100 parts by weight of said solution, the hypophosphite ion being present in an amount not substantially in excess of about 3 parts by weight to about 100 parts by weight of said solution; immersing a suitable substrate material in said solution; maintaining said solution within a temperature range from about 70° C. to about 90° C.; decreasing the pressure on said solution to a value below the ambient atmospheric pressure and above the vapor pressure of said solution; and plating said substrate material by autocatalytic reaction of said nickel salt and said hyphosphite salt.

7. An improved process for the electroless plating of nickel from a transport controlled system comprising the steps of: providing an aqueous solution maintained at a pH value in the range from about 3 up to about 7, said solution including a nickel salt and an alkaline hypophosphite; immersing a suitable substrate material in said solution; maintaining said solution within a temperature range from about 70° C. to about 90° C.; decreasing the pressure on said solution to a value below the ambient atmospheric pressure and above the vapor pressure of said solution; and plating said substrate material by auto-catalytic reaction of said nickel salt and said hypophosphite salt.

8. An improved process for the electroless plating of nickel from a non-transport controlled system comprising the steps of: providing an aqueous solution maintained at a pH value in the range of about 4 to about 5.6, said solution including a nickel salt and an alkaline hypophosphite; immersing a suitable substrate material in said solution; applying pressure above the ambient pressure thereon and plating said substrate by auto-catalytic reaction of said nickel salt and said hypophosphite salt.

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