Super High Speed Electroless Nickel Plating Process.

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A SUPER high speed electroless nickel plating process has been developed that gives the deposition rate of 23-27 μ m/h in stable conditions. Attempt was made to study the effect of parameters like, nickel sulphate, sodium hypophosphite, succinic acid, complexing agent CL-1, accelerator AL-1, pH, bath temperature and time etc. on the rate of electroless nickel plating. The corrosion resistance of nickel deposit was determined by usual method. Microstructure and crystallinity of nickel deposit were determined by metallography, scanning electron microscopy and X-ray diffractometry.

With the extensive use of EN plating there is a growing demand by engineering Industries such as mechanical, electronics, chemical and printing for thicker deposits of EN. In order to improve production efficiency, super high speed electroless nickel plating with deposition rate of 23-27 μ m/h becomes a new area of interest in EN plating technology.

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Introduction:

Because of its excellent corrosion resistance, wear resistance, solderability, low porosity, uniform thickness even on complex parts, and ability to plate on nonconductors, electroless nickel (EN) plating is widely used in engineering industries such as oil, chemical, plastics, optical parts, printing, aerospace, automobile, electroless, textile, ship making, and food.{1,3} The deposition rate of regular acidic EN plating, using sodium hypophosphite as the reducing agent, is usually in the range 13–17 μ m/h. {2} If the deposition rate is between 18–22 μ m/h, the process is called high-speed EN plating. {7, 9} As the use of EN plating becomes more extensive in engineering industries, there is a growing demand for thicker deposits of nickel plating. In addition, because of the need to improve production efficiency, super-high-speed, electroless nickel plating with deposition rates of 23–27 μ m/h has become a new area of interest in EN plating technology. {15}

Many factors affect the deposition rate in EN plating processes: bath temperature and PH, the concentration of Ni2+ ions and sodium hypophosphite, bath loading, and the type of complexing agent, accelerator, and stabilizer used. {12, 13, 14} There are two ways to improve the deposition rate of EN plating. The first method is to change the complexing agent so that the activation energy needed for reducing the Ni2+ complex ion will decrease. {10} The complexing agents used in EN plating are primarily hydroxy acids, lactic acid, malic acid, citric acid, and glycolic acid. These organic hydroxy acids can form one or more chelating complexes with nickel ions. The number depends on the concentration and structure of the complexing agent and the bath PH. {4} If one complexing agent is used, the deposition rate follows this trend, from lowest to highest {5}: succinic acid, glycolic acid, lactic acid, salicylic acid, glycine and tartaric acid. It is suggested in the literature that lactic acid is a good complexing agent because it coordinates, buffers, and accelerates the plating rate well. {16} if two complexing agents are used, both of them can coordinate with ions and a mixed, ligand coordination compound will be formed. This can decrease the activation energy. In addition, complexing agents have different characteristics when they are used together and surprising results may be obtained. {6} For example, when an acetate citrate EN bath is used, the deposition rate is usually about $10-13\mu$ m/h. K. Parker{3} studied the deposition rate when a second complexing agent was added. He reported that if propionic acid is added to acetic acid, the deposition rate will improve from 11 μ m/h to 15–16 μ m/h. Adding the second complexing agent not only improved the deposition rate, but it also improved the bath stability and the tolerance of the bath to phosphite build-up. {7}.

The second way of improving the deposition rate of EN plating is to add a suitable amount of accelerator exaltant. G.Gawrilov{8} proposed that fluoride can be used as an accelerator. A small amount of fluoride can slightly improve the deposition rate and promote deposition on aluminum. But higher amounts of fluoride increase the internal stress. In recent years, the use of organic accelerators has attracted more attention. Three kinds of organic accelerators are commonly used: (i) saturated monocarboxylic acids and their salts, (ii) saturated amino acids, and (iii) saturated, non-substituted dicroboxylic acids. Of these, dicarboxylic acid has the widest application. It can improve the deposition rate from $11-16 \mu m/h$. If a better complexing agent is selected, it can result in even higher deposition rates. McGean-Rohco Inc. of Japan Mineral Corporation reported a deposition rate of 20 $\mu m/h$ with this process. {13}

My consistent study of EN plating processes, such as Ni-P of high and low phosphorous and Ni-B using DMAB as a reducer, lead me to develop a super high-speed, EN plating process with a deposition rate of $23-27 \mu$ m/h using a special complexing agent, accelerator, and stabilizer. This process is likely to have wide applications in many industrial fields.

Experiment Parameters {15}:

Optimized bath composition:

Nickel sulphate	35 g/l
Sodium hypophosphite	25 g/l
Succinic acid	20 g/l
Complexing agent CL-1	45 ml/l
Accelerator AL-1	30 ml/l
pH	5–6
Temperature	90/95 °C
Bath loading	$1-1.5 \text{ cm}^2/l$
Deposition rate	25–28 µm/h
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The process for making the bath:

(i) Weigh out the amounts of nickel sulphate, sodium hypophosphite, succinic acid, and complexing agent CL-1 specified above and dissolve them in 800 ml of distilled water by stirring.

(ii) Add 30 ml of accelerator AL-1.

(iii) Adjust the PH value to 5.8 using ammonia and enough water to make up 1 liter.

Methods of determination:

(i) EN plating: Put the bath in a beaker and heat the beaker in a thermostatic jar. Measure the deposition rates by the increase of sample weight with standard area per unit of time. (ii) Determining corrosion resistance: Put the sample in the solutions of NaCl, H2So4, HCl, and NaOH respectively. Observe the corrosion over different time periods. (iii) Determining deposit morphology: By Scanning Electron Microscopy (SEM). (iv) Determining crystalline state of the deposit: By Japan RikaguD/Max- $\lambda\beta$ X-ray diffraction instrument.

Results:

1. Effects of Bath composition and operating conditions on deposition rate:

To select the optimum bath composition and operating condition, variation of one bath component or condition at a time while keeping the others constant.

The following are the results. {15}:

Nickel sulphate

The Ni²+ ion concentration determined the composition of the nickel complex ion and the stability of the bath. The variation in the deposition rate as with varying the nickel sulphate concentration from 15 g/l to 75 g/l is illustrated in [Fig 1]. It shows that with an increasing concentration of nickel ions, the deposition rate increases, reaches its highest point, and then decreases. When the concentration of nickel sulphate is 60 g/l, the bath becomes turbid because of hydrolysis of Ni²+. Therefore, the concentration of Ni²+ ions should be controlled below 60 g/l. 35g/l is the optimum concentration.

Sodium hypophosphite

Sodium hypophosphite as the reducing agent and the source of phosphorous in the alloy. [Fig 2] illustrates the variation in the deposition rate with the variation in the sodium hypophosphite concentration from 16 g/l to 45 g/l. [Fig 2] shows that the deposition rate increases as the concentration of sodium hypophosphite increases. However, when the concentration reaches 45 g/l, the bath becomes unstable and decomposes. As a result, the concentration of sodium hypophosphite should not exceed 45 g/l. 25 g/l is the optimum concentration.

Succinic acid

Succinic acid is used for coordination, acceleration, and buffering. [Fig 3] illustrates the variation in the deposition rate as the concentration of succinic acid varies from 5 g/l to 35 g/l. [Fig 3] shows that with an increasing concentration of succinic acid, the deposition rate first increases, and then decreases. The highest point is at a concentration of 20 g/l, which is the optimum concentration.

Complexing agent CL-1

Complexing agent CL-1 can form a stable coordination compound with Ni²+, which makes Ni²+ stable in the bath. [Fig 4] illustrates the variation of the deposition rate as the concentration of CL-1 increases from 22.5 ml/l to 75 ml/l. The results show that the deposition rate decreases, while the stability of the bath increases, with increasing concentrations of CL-1. Considering both rate and stability, 45 ml/l is the optimum concentration.

pН

[Fig 5] illustrates the variation of the deposition rate as the PH value varies. [Fig 5] shows that the deposition rate increases with increasing PH. Bath PH has a great effect on deposition rate. One possible reason is that some of the coordinated water dissociates into hydroxyl, which acts as an electron bridge and accelerates the transmission of electrons. The deposition rate is highest with a PH value of 5.8. When the PH value is above 5.8, some of the nickel coordination compounds begin to hydrolyze. When the PH value is even higher, the bath tends to precipitate. This causes the concentration of Ni²+ to drop and the deposition rate to decrease.

Bath Temperature

[Fig 6] illustrates the variation in the deposition rate as the temperature varies. The deposition rate is very low at 70 °C. After 80 °C, the deposition rate increases markedly

and the rate increases linearly with increasing temperature. The bath becomes unstable when the temperature is above 98 °C. The bath temperature is typically controlled between 90–95° C.

Plating time

[Fig 7] illustrates the variation of the deposition rate as the plating time varies. [Fig 7] shows that in the first hour of plating, the variation of the deposition rate is very small. After one hour, the deposition rate decreases slowly because of the consumption of various bath components. Therefore, the bath should be replenished and the PH value adjusted for longer plating times to keep the deposition rate within a suitable range.

Accelerator AL-1

During dipping of the samples in a series of baths with the same components except for the concentration of the accelerator and measured the deposition rate with the gravimetric method, the results are shown in [Fig 8]. When the concentration of accelerator AL-1 is 0–4.5 ml/l, the deposition rate increases sharply with increasing concentrations of accelerator. 4.5–110 ml/l is a constant area. When the concentration is above 110 ml/l, deposition rate decreases sharply and when the concentration reaches 120 ml/l, EN plating ceases.

2. The corrosion resistance of super-high-speed EN plating:

Table 1 illustrates the corrosion rates of the EN plating in different corrosive media. It shows that super-high-speed EN deposit has better corrosion resistance in sulphuric acid and hydrochloric acid than in the other three systems. While in sodium chloride and sodium hydroxide solutions, its corrosion resistance can match the other three systems. While the concentration of chloride, sulphuric acid, hydrochloric acid, and sodium hydroxide is rather high, the samples plated with super high speed EN were not affected in 12 days. This demonstrates that super-high-speed EN has excellent corrosion resistance in these solutions.

* Composition of (a): Nickel sulphate 30g/l, Sodium acetate 15g/l, Sodium citrate 15g/l, Sodium hypophosphite 20g/l, pH 4.5 and T=90°C.

** Composition of (b): Nickel sulphate 25g/l, Lactic acid 3g/l, Sodium fluoride 1g/l, Sodium hypophosphite 20g/l, pH 4.5 and T= 90°C.

*** Composition of (c): Nickel sulphate 25g/l, Succinic acid 16g/l, Malic acid 24 g/l, Sodium hypophosphite 24 g/l, Lead acetate 0.003g/l, pH 5.8 and T=90°C.

3. Surface topography of super high speed EN plating.

The examination was done on surface topography for electroless nickel deposits from a super high-speed acidic bath and a common citrate-acetate bath under a scanning electron microscope (SEM) at magnifications of 1200 and 1000 respectively. These observations showed that the maximum diameter of the crystal of the acidic high-speed EN deposit Is 7.0 μ m—much less than that of the citrate-acetate bath, which is 12 μ m. This shows that the complexing agent we chose enabled us to obtain a dense deposit with finer grains. It is reported in the literature that Ni-P deposit has amorphous structure. {16}

Conclusions:

(A): Based on these studies, the optimum composition of the EN bath is: Nickel sulphate 35 g/l, Succinic acid 20 g/l, Sodium hypophosphite 25 g/l, Complexing agent CL-1 45 ml/l, accelerator AL-1 30 ml/l, PH 5–6, temperature 90–95°C and bath loading 1–15 dm²/l.

(B): Super-high-speed EN deposit has excellent corrosion resistance in solutions of NaCl, H2So4, HCl, and NaOH.

(C): The maximum diameter of the super-high-speed EN crystal is 7 μ m, while that of common acetate bath is 12 μ m, which shows that the super-high-speed EN deposit is denser.

(D): Super-high-speed EN deposit shows non- crystalline structure.

Bath/results/corr.	Super high speed	Citrate Acetate	Lactic acid-Boric	Succinic acidand
media	EN bath	bath(a) *	acid bath(b)**	malic acid bath(3)***
10% Nacl solution	No change in 12	No change in 12	No change in 12	No change in 12 days
	days	days	days	
10% H2So4 Sol.	No change in 12	Turns to be blue in	Turns to be blue in	Turns to be blue in 10
	days	10 days	10 days	days
10% HCl	No change in 12	Turns to be blue in	No change in 12	Turns to be blue in 8
	days	19 days	days	days
10% NaOH	No change in 12	No change in 12	No change in 12	No change in 12 days
	days	days	days	

Table I – Corrosion resistance in different kinds of corrosive media.

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