

# The Effect of Nickel Salts on Electroless Nickel Plating

By Konrad Parker

**Nickel chloride, fluoride, bromide, iodide, formate, acetate, sulfamate, fluoborate, borate and sulfate were compared in an acid lactate-acetate electroless nickel plating solution formulation for plating rate and bath stability, as well as nitric acid resistance and hardness of the deposit.**

In previous experiments, the effect of monovalent cations ( $\text{NH}_4^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) on electroless nickel (EN) plating was investigated.<sup>1</sup> The effects of various chelating agents in EN baths has been extensively studied.<sup>2-4</sup> No systematic comparison of different nickel salts in an acid EN plating solution has been published, however, except for residual internal stress measurements of EN-plated strips by the author.<sup>5</sup> It was found that in 25- $\mu\text{m}$  EN deposits containing 8 to 10 percent phosphorus from a lactate bath, nickel chloride produced higher stress than the sulfamate, while nickel sulfate coatings had the lowest stress. Other experiments compared three nickel salts in an alkaline ammonium citrate bath. In the temperature range of 20 to 50 °C, the sulfate was found to plate slightly faster than the sulfamate and about 10 percent faster than the chloride.<sup>6</sup>

The first EN plating solutions used by Brenner and Riddell in 1944 were prepared with nickel chloride.<sup>7</sup> Later, the Kanigen<sup>®</sup> process and proprietary EN plating solutions employed nickel sulfate almost exclusively in acid EN plating formulations.<sup>8</sup>

Patents have been granted for EN plating solutions containing fluoride ions, based on either faster plating rate<sup>9,10</sup> or greater deposit hardness.<sup>11</sup> The use of nickel ammonium fluoride<sup>12</sup> and nickel fluoborate<sup>13</sup> has also been patented.

At present, commercial acid EN plating solutions are made up with nickel sulfate; however, most alkaline baths contain nickel chloride or nickel sulfamate. The experiments re-

ported here were designed to evaluate and compare various non-complexing nickel salts in a generic EN plating formulation.

## Experimental Procedure

The EN plating was performed on clean, mild steel coupons (20  $\text{cm}^2$  surface area) in 200-mL solutions, in a constant temperature bath at  $90 \pm 1$  °C. The following formulation, similar to that used in previous work, was used in all experiments:

Nickel salt	0.1 M
Lactic acid	0.3 M
Sodium acetate	0.25 M
Sodium hypophosphite	0.3 M
Sodium hydroxide	0.2 M
Lead ion	0.5 ppm

All solutions were initially adjusted to pH 4.8–4.9. Most of the chemicals were obtained from commercial sources—the nickel salts as purified, liquid concentrates, except for the borate, formate and fluoride, which were prepared *in situ* from nickel carbonate and the appropriate dilute acid.

Plating rates were calculated from the weight gain of the plated coupons. The EN bath stabilities were determined by measuring the elapsed time to decomposition (black solution) after the addition of 2.0 mL of 100-ppm palladium solution to 100 mL plating bath aliquot at 60 °C on a magnetic stirrer-hot plate. The nitric acid resistance was evaluated by a 30-sec partial immersion of the plated coupons in the concentrated acid. The buffering capacity of the nickel salts was determined by pH measurements of the solutions after plating. The hardness of some EN deposits was measured on

a digital microhardness tester<sup>a</sup> using a Knoop indenter with a 100-g load. Phosphorus content of the Ni-P coatings was determined by X-ray fluorescence with an XDVM<sup>b</sup> having an accuracy of  $\pm 1$  percent.

## Results and Discussion

All of the experimental results are shown in the table. The nickel sulfate, chloride and ammonium sulfate solutions had essentially the

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Nickel salt	Plating Rate $\mu\text{m/hr}$	Palladium Stability sec	pH Change	Nitric Acid Resistance	Hardness $\text{HK}_{100}$	%P
Sulfate	19	12	-0.3	OK	580	7.3
Chloride	19	12	-0.3	shadow	550	5.8
Fluoride	16	12	-0.1	exc.	650	8.3
Bromide	15	150	-0.2	shadow		
Iodide	3	600+	0	shadow		
Formate	16	12	0	OK		
Acetate	16	12	-0.1	black		8.8
Ammonium sulfate	18	12	-0.2	OK		
Sulfamate	16	20	-0.3	shadow		5.8
Fluoborate	15	15	-0.3	shadow		8.0
Borate	23	12	0	OK		5.5

<sup>a</sup> Micromet II, Buehler Ltd., Lake Bluff, IL

<sup>b</sup> Fischerscope, Fischer Technology, Windsor, CT

same plating rates. The only nickel salt producing a faster rate was the borate, probably a result of its buffering effect.

Comparing the nickel halides, the plating rates decreased in the following order: Cl<sup>-</sup>, F<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, whereas the bath stabilities increased in the same order. Accordingly, the nickel iodide solution had by far the best palladium stability, but also the slowest plating rate. The nickel fluoride bath deposited a coating with excellent nitric acid resistance and hardness.

The plating rates of the other nickel salts evaluated decreased in this order—sulfate, acetate, formate, sulfamate, fluoborate. All the deposits were bright except for the nickel formate coating, which was dull. The nickel acetate deposit had the least nitric acid resistance.

It is noteworthy that the plating rates of the various nickel salt EN solutions decrease in the opposite order of their solubilities. Accordingly, nickel iodide is the most soluble, but the slowest plating; the opposite is true for nickel borate.

#### Conclusions

Because for most EN applications, the plating rate and cost are the most important considerations, the nickel sulfate salt is the best choice for the formulator and plater. If needed, boric acid or sodium borate could be added to maintain the bath pH and possibly increase the plating rate. When increased as-plated hardness is desired, the use of nickel fluoride or the addition of a fluoride salt to the EN bath should be considered. This should also improve the nitric acid resistance of the deposit; however, all such formulation changes or additions must be carefully evaluated for their effect on deposit properties.

#### Summary

The performance of various non-complexing nickel salts was compared in an acid EN plating solution formulated with lactic acid as the complexing agent and sodium hypophosphite as the nickel reducing agent. The plating rates of the nickel sulfate, nickel ammonium sulfate and nickel chloride plating baths were about equal. The nickel halide solution rates decreased as follows: Cl<sup>-</sup>, F<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, whereas their bath stabilities increased in the same order. The nickel sulfamate, acetate, formate and fluoborate induced slower plating rates, while the nickel borate plated appreciably faster than the nickel sulfate solution. Evaluation of the EN deposits found the nickel fluoride to yield the highest hardness and best nitric acid resistance.

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