By Glenn O. Mallory and Konrad Parker

The effect of increasing concentrations of  $NH_4^*$ ,  $Li^*$ ,  $Na^*$ and  $K^*$  on plating rate and bath stability were investigated in a lactate-acetate EN plating solution. The relationship between sulfate and phosphite salt solubilities and metal turnovers was studied. Deposition potentials, microstructures and phosphorus contents were also determined.

ince its industrial development in the 1950s, electroless nickel (EN) has found increasing use on a wide variety of parts, primarily for functional engineering applications requiring corrosion and/or wear resistance. Although its growth has slowed in the last few years, the total value of EN coatings in the U.S. is estimated at \$200 million.<sup>1</sup>

EN plating has three major disadvantages compared to electrolytic nickel plating:

- High chemical cost (\$0.40 to 0.70/L)
- Limited plating bath life (3 to 6 MTO)
- Expensive spent bath treatment or disposal

Limited bath life is the result of continuous accumulation of phosphite and sulfate salts as by-products of the plating reaction. To maintain the optimum pH, frequent addition of alkali is necessary. The main reactions are:

(1) Reduction NiSO<sub>4</sub> + 3MH<sub>2</sub>PO<sub>2</sub>  $\rightarrow$  Ni<sup>0</sup> + 2MH<sub>2</sub>PO<sub>3</sub> + MHSO<sub>4</sub> + P +  $^{1}/_{2}$ H<sub>2</sub>

(2) pH adjustment (4.5 to 6.0) 2MOH +  $MH_2PO_3 + MHSO_4 \rightarrow M_2HPO_3 + M_2SO_4 + 2H_2O$ 

Table 1 shows the rapid increase in salt concentration with each nickel turnover (MTO = 1, initial nickel concentration is replenished once) in a typical EN plating bath containing nickel sulfate, sodium hypophosphite and sodium salts of organic acids with potassium carbonate as the pH adjuster.

It is the increase in salt content that increases the density and viscosity of the solution, decreases the plating rate and induces the precipitation of nickel phosphite. The properties

Table 1 Salt Concentrations in mol/L						
МТО	[SO <sub>4</sub> -2]	[HPO <sub>3</sub> -2]	[Na⁺]	[K⁺]		
0	0.1	0	0.6	0		
1	0.2	0.27	0.9	0.2		
2	0.3	0.54	1.2	0.4		
3	0.4	0.81	1.5	0.6		
4	0.5	1.08	1.8	0.8		
5	0.6	1.35	2.1	1.2		
6	0.7*	1.62**	2.4	1.2		
* 100 g Na <sub>2</sub> S0 ** 200 g Na <sub>2</sub> HF	D <sub>4</sub> PO <sub>3</sub>					

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of the Ni-P deposit deteriorate, as evidenced by increasing porosity and tensile stress. Blistering on aluminum is common after three MTOs.

The solubilities of alkali phosphite and sulfate salts are shown in Tables 2 and 3. As expected, the ammonium salts are most soluble. The nickel and lithium phosphites have the lowest solubilities in water. Because a mixture of sodium and potassium sulfates is present in the used plating bath, the actual phosphite solubilities are lower than in water alone. The nickel phosphite solubility depends on the chelating acids used in the EN formulation, and which control the "free nickel" ion concentration.<sup>2</sup>

Sodium and potassium sulfate often crystallize when the spent bath is stored below 5 °C. The phosphite anion can be precipitated as the calcium or magnesium salt; however, the plating solution will then contain calcium or magnesium cations that impair deposit properties.<sup>3</sup> The use of lithium salts in an EN bath has not been previously reported. In an electroless copper bath, lithium hydroxide was found to be superior to sodium and potassium hydroxide with regard to improving the plating rate and the mechanical properties of the copper deposits.<sup>4</sup> One early reference found a sodium

## Table 2 Solubilities of Monovalent Salts Of Phosphorous Acid

Phosphite	Solubi 0°C	ility, g/L Other
$NH_4(H_2PO_3)$	620 1710	750 <sub>40°</sub> 2600*
Li <sub>2</sub> HPO <sub>3</sub>	90	30 <sub>100°</sub>
Na <sub>2</sub> HPŎ <sub>3</sub>	800	1000 <sub>50°</sub>
NaH <sub>2</sub> PO <sub>3</sub> · ⁵/₂H₂O	500*	1930 <sub>42°</sub> *
KH <sub>2</sub> PO <sub>3</sub>		2200 <sub>30°</sub> *
NiHPO3	7	3 <sub>100°</sub>

\*Source: Handbook of Chemistry and Physics, CRC Press.

# Table 3 Solubilities of Monovalent Salts Of Sulfuric Acid

Sulfate	Solubility, g/L 0°C 100 °(		
(NH <sub>2</sub> ) <sub>4</sub> SO <sub>4</sub>	706	1038	
Li <sub>2</sub> SO <sub>4</sub>	261	230	
Na <sub>2</sub> SO <sub>4</sub>	48	427	
K <sub>2</sub> SO <sub>4</sub>	120	241	
NiSO <sub>4</sub>	293	837	

\*Source: Handbook of Chemistry and Physics, CRC Press.

# Table 4 Generic Plating Formulations

MTO-0 Nickel Sulfate Lactic acid Acetic acid M Acetate Hypophosphorous acid Lead		M 0.102 0.306 0.25 0.25 0.306 0.5 ppm
MTO-3 Add M <sub>2</sub> SO <sub>4</sub> Phosphorous acid MOH	to pH	0.306 0.84 4.6
MTO-6 Add $M_2SO_4$ Phosphorous acid MOH $M = NH_4^+$ , Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup>	to pH	0.612 1.68 4.6

glycolate bath to plate at 21 $\mu$ m/hr at 97 °C and an initial pH of 4.5, compared to a rate of 16  $\mu$ m/hr for an ammonium glycolate bath.<sup>5</sup>

This investigation explores the effect of varying the monovalent alkali ions in an EN plating solution.

### **Experimental Procedure**

For all plating experiments, 4-L solutions were used. Because only the sodium salts of hypophosphorous acid are commercially available, the other alkali hypophosphites were prepared *in situ* from the acids by neutralization with the appropriate alkali or ammonium hydroxide. The initial and simulated three- and six-turnover generic formulation baths are as shown in Table 4.

The three- and six-MTO baths were prepared from MTO-0 by adding the calculated amounts of sulfuric and phosphorous acids, neutralized with the respective alkali or ammonia to obtain the desired salt concentrations. Plating was performed in thermostatically controlled 4-L Pyrex<sup>TM</sup> beakers. The initial pH of all baths was 4.6. Plating was carried out at 87 °C ±2 for 1 to 2 hr. Plating rates were determined by measurement of deposit thickness. Initial deposition poten-

# Table 5 Plating Solutions without Sulfate

Constituent	Concentr MTO-0	ation, M MTO-6
Nickel hypophosphite	0.102	0.102
Hypophosphorous acid	0.102	0.102
Lactic acid	0.306	0.306
Acetic acid	0.25	0.25
K acetate	0.25	0.25
Phosphorous acid	_	1.68
Lead, ppm	0.5	0.5
КОН	to p⊢	4.6
Temperature	87 ± 2	°C

tials were measured against Ag/AgCl with a digital multimeter at 85 °C. Deposit composition was obtained by foil analysis using an electron beam microprobe (EDS). Intrinsic stress measurements were made with a spiral contractometer. The MTO-0 deposit crystal structures were examined on foils with an X-ray diffractometer. Plating solutions containing potassium salts, but no sulfate ions, were prepared and evaluated as listed in Table 5.

### **Results and Discussion**

The results of the initial experiments are shown in Table 6. The plating rates of all the baths decreased by about 30 percent after three metal turnovers. Surprisingly, the fastest initial plating rate was observed in the lithium bath, which produced a deposit with relatively low potential and slightly higher phosphorus content.

The ammonium bath plated the slowest; however, it yielded six turnovers without precipitation. Both results can be attributed to the nickel complexing action of ammonia. Tensile stress increased considerably with turnovers in deposits from the ammonium and potassium baths. Comparison of X-ray diffraction diagrams of the MTO-0 foils reveals no microstructural differences among the various cation deposits (Table 7).

In the absence of sulfate, the potassium plating bath initially plated 12.5  $\mu$ m/hr. After addition of 1.68 M potassium phos-



Fig. 1—Solubility of anhydrous phosphites.







Fig. 3—Lithium phosphite removal.

# Table 6 Plating Experiment Results

		NH₄⁺			Li⁺			Na⁺			K⁺	
МТО	0	3	6	0	<b>3</b> ª	<b>6</b> <sup>ь</sup>	0	3	6°	0	<b>3</b> ⁴	<b>6</b> <sup>b</sup>
Plating rate, μm/h	13	9	5	19	_	_	15	11	_	13	9	_
Phosphorous content, wt %	9.6	9.9	10.0	10.2	-	-	10.0	10.1	-	10.1	10.3	_
Intrinsic stress, KSI	0.02	0.28	8.3	-0.03	-	-	0.07	0.3	-	-2.2	3.2	_
MPa	0.14	2	58	-0.2	-	_	0.5	2	-	-15	22	-
Initial deposition potential mV (86 °C)	-604	-606	-610	-589	-	-	-590	-602	-	-597	-614	-

a. Precipitate forms at 85 °C

b. Not run

c. Precipitate forms after about 30 min of plating

d. Light precipitate forms during make-up; dissolves on heating

Table 7 Summary of X-ray Data					
Sample	d, Å	D, Å			
NH <sub>4</sub> <sup>+</sup> , MTO-0	2.01	14			
NH₄⁺, MTO-3	2.01	15			
NH <sub>4</sub> <sup>+</sup> , MTO-6	2.01	13			
Li⁺, MTO-0	2.01	15			
K⁺, MTO-0	2.01	15			
Na⁺, MTO-0	2.02	15			

# Table 8 Lithium Phosphate Removal 1.75 MTO

Constituent	Initial Conc w/sulfate	entrations, M w/o sulfate
NiSO,	0.102	
Ni(H <sub>2</sub> PO <sub>2</sub> ) <sub>2</sub>		0.102
H <sub>3</sub> PO <sub>2</sub>	0.102	0.102
Lactic acid	0.306	0.306
Acetic acid	0.25	0.25
Li acetate	0.25	0.25
Li <sub>2</sub> SO <sub>4</sub>	0.275	
H <sub>3</sub> PO <sub>3</sub>	0.47	0.47
Lead	3.86 x 10⁻6	3.86 x 10⁻6
LiOH	to pH 4.6	to pH 4.6
Temperature	≥ 95 °C	≥ 95 °C

phite (6 MTO), the plating rate decreased to 5  $\mu$ m/hr. The deposition potential also decreased from -590 to -620 mV.

Because of the limited solubility of lithium phosphite compared to the other monovalent cation phosphites (Figs. 1 and 2), the possibility of phosphite reduction in a used lithium plating bath was investigated. A 1.75 MTO solution was simulated with lithium acetate, sulfate and hydroxide (Table 8). Filtration at 95 °C through a 0.5- $\mu$ m membrane reduced the phosphite content from 39 to 30 g/L and increased the plating rate from 16.3 to 17.5  $\mu$ m/hr. It may be possible to remove part of the accumulating phosphite during plating by continuous filtration, as shown in the diagram of Fig. 3. The operating life of the lithium bath would thereby be extended and the plating rate increased.

### Summary

Electroless nickel plating solutions containing lactic and acetic acids as complexant and buffer were prepared with hypophosphorous acid and ammonium, lithium, sodium or potassium hydroxide at 0, 3 and 6 metal turnovers. At 87 °C and pH 4.6, the lithium bath had an appreciably faster initial plating rate, but it precipitated after a few metal turnovers. The ammonium bath had the slowest initial plating rate; however, it was the only solution that plated at six metal turnovers without precipitation. The removal of lithium phosphite by

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filtration during plating to extend the life of an EN plating bath warrants further investigation.

# Findings

The four monovalent cations investigated show a diverse effect on the operation of an electroless nickel plating system. The potassium bath is limited by the low solubility of the accumulated potassium sulfate. Sodium ions have a similar effect on the process at greater MTOs, but for different reasons. In the all-sodium bath, nickel phosphite is the principal precipitate, at about three MTOs.

When ammonium ions are used, it is evident that the complexing effect of the amine group with nickel enhances the solubility of nickel at the expense of nickel phosphite precipitation. Also, the ammonium ion increases the solubility of the sulfate anion relative to sodium and potassium sulfate. The rate of deposition is decreased, however, with increased  $NH_{a}^{+}$  concentration.

Finally, the lithium ion has two positive effects on the EN plating system. First, the rate of deposition increases in the all-lithium bath. Second, and most importantly, it was seen that the low solubility of dilithium phosphite ( $Li_2HPO_3$ ) at temperatures in excess of 88 °C can be used to control the accumulation of orthophosphite in the EN plating bath to about one MTO.

## References

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## About the Authors

Glenn O. Mallory is a founder of Electroless Technologies Corp. (ETC), 3860 Cloverdale Ave., Los Angeles, CA 90008. He is a specialist in electroless deposition with more than 30 years' experience in the surface finishing industry. He is a former vice-president of R&D for electroless nickel development at Allied-Kelite Div. of Witco Chemical Corp. He holds a BS from UCLA and an MS from California State University, Los Angeles.

Konrad Parker is a specialist in electroless nickel plating. A graduate of Illinois Institute of Technology with an MS degree, he holds many patents and is the author of numerous papers, including "The Formulation of Electroless Nickel-Phosphorus Plating Baths," for which he received the AESF Gold Medal in 1988.