Metal Recovery from Spent Electroless Plating Solutions By Oxalate Precipitation

By O. Gylienė and M. Šalkauskas

It is possible to recover metals from spent electroless plating solutions by an unusual process that results in a very high percentage of recovery. Oxalate precipitation was studied to determine conditions for recovery without waste or destruction of the complexing agents.

Electroless plating solutions contain chelated metal components. Such complexes hinder metal recovery as insoluble compounds, particularly as hydroxides, to the extent that the complexing ability of most complexing agents increases with increasing pH.

Clyde S. Brooks proposed oxalate precipitation for Ni, Cu, and Co recovery from spent electroless plating solutions.[1] After destruction of the organic complexing agents by aeration, oxalic acid, in an amount from 1.5 to 2 times the stoichiometric requirement, was added at pH 5 to 6. Insoluble metal oxalates were separated by filtration.

The objective of this study was to find optimal conditions for metal (Cu, Ni, Co) removal from spent electroless plating solutions, by means of oxalate precipitation, without destruction of the complexing agents.

Experimental Procedure

All experiments were carried out at room temperature by addition of oxalic acid to metal-containing solutions. The pH of the solutions was adjusted with H_2SO_4 or NaOH. Experiments were carried out with KOH, also, because of the low solubility of sodium oxalate, compared with potassium oxalate. The results indicate that the low solubility of sodium oxalate does not affect the metal oxalate precipitation process.

Oxalate precipitates were separated by filtration after two to five days. Metals in the filtrate were determined by titration with EDTA, in small quantities, photometrically.

Table 1
Removal of Some Metals from Acidic Solutions (Beginning metal conc., 0.1 mol/L)

	Concentration	Percent metal removal		
Acid	mol/L	Cu(II)	Ni(II)	Co(II)
H_2SO_4	1.8	99.8	53	30
	3.5	99.7	10	0
	7.0	99.5	0	0
HNO_3	3.5	99.9	20	5
	7.0	99.9	17	0
	13.0	99.9	98	47
HCl	3.0	90	75	3
	6.0	25	12	0
	12.0	0	0	0
H_3PO_4	1.7	99.9	100	99.2
	3.3	99.9	99.8	99.4
	5.0	99.9	99.8	99.4

Results and Discussion

The results obtained for removal of Cu(II), Ni(II), and Co(II) from strongly acidic solutions are listed in Table 1. As shown, the largest amounts of metals are removed from phosphoric acid solutions. The concentration of this acid does not affect the extent of metal removal, which approaches 100 percent. The concentration of hydrochloric acid, however, which is the most important and widely used acidifier, hindered the removal of metals from its solutions. The effect of the concentration of nitric and sulfuric acids on removal of Ni(II) and Co(II) is noticeably greater than on Cu(II) removal.

To investigate the forming of insoluble metal oxalates with rise in pH, oxalic acid was added to metal-containing solutions. The results are shown in Table 2. The dependence of the solubility of metal oxalates on pH is complicated. By any consideration, the solubility of metal oxalates at low pH is much less than in neutral solutions. In basic solutions, the solubility of copper oxalate is high, while the solubility product of copper hydroxide is low. This is possible because of the complexing ability of oxalate.

The most important factor for residual metal concentration is the starting metal concentration (Table 3). With increasing starting concentrations of metal ion, the residual metal concentrations decrease (*i.e.*, the extent of recovered metal increases).

In this study for electroless plating, Ni-glycine (aminoacetic acid), Ni-citrate, Co-glycine, Co-citrate, Cu-tartrate, and

Table 2
Influence of pH on Residual Metal Concentration After Oxalate Precipitation (Beginning metal conc., 0.1 mol/L)

$H_2C_2O_4$ mol/L	pH	Residual Metal Conc., mg/L		
		Cu(II)	Ni(II)	Co(II)
0.1	0	110	100	90
	1	125	220	120
	2	70	740	300
	3	62	300	290
	4	90	270	270
	5	210	300	280
	6	180	20	45
	7	320	27	12
	8	450	3	3
	9	640	3	2
0.3	0	13	1	7
	1	27	7	5
	2	640	23	50
	3	770	440	400
	4	730	460	400
	5	700	660	800
	6	570	140	90
	7	700	30	15
	8	700	2	3
	9	640	1	2

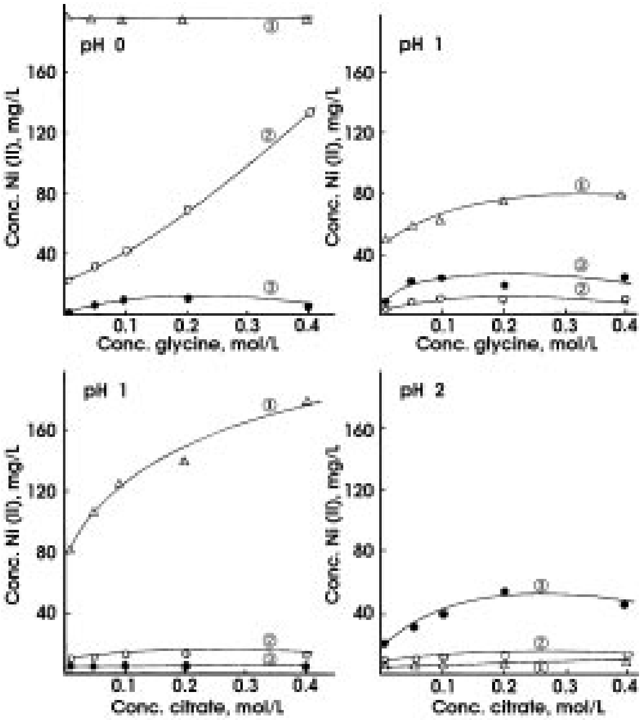

Fig. 1—Dependence of residual nickel concentration on concentration of complexing agents (glycine and ammonium citrate) after oxalate precipitation. Ni(II) conc. (mol/L): 1 - 0.01, 2 - 0.05, 3 - 0.1.

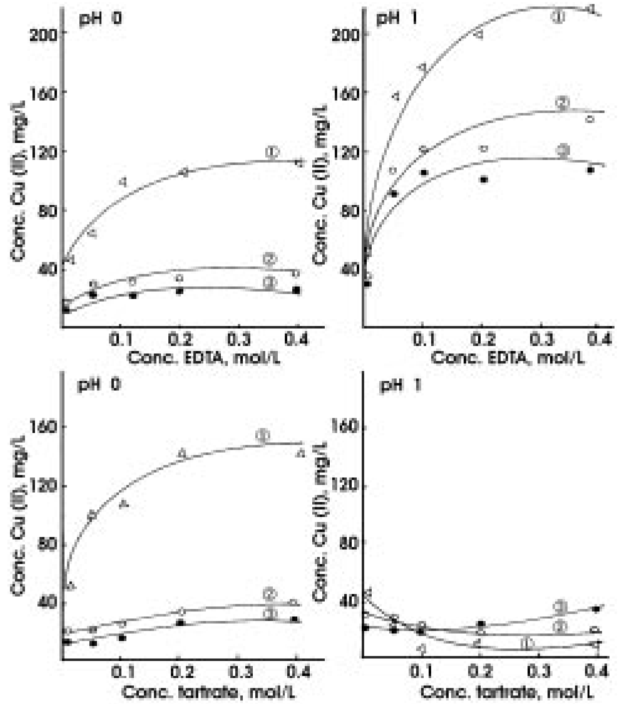

Fig. 2—Dependence of residual copper concentration on concentration of complexing agents (EDTA and tartrate) after oxalate precipitation. Cu(II) conc. (mol/L): 1 - 0.01, 2 - 0.05, 3 - 0.1.

Cu-EDTA complexes were used to examine the influence of complexing agents on precipitation of metal oxalates. Molar oxalic acid concentration in all cases was three times higher than the metal ion concentration.

The dependence of residual nickel concentrations on complexing agent concentrations is shown in Fig. 1. The low residual nickel concentrations are obtained at pH 1–2 and starting nickel concentration at 0.01 mol/L. The effect of complexing agent concentration in most cases is negligible. Only at small (0.01 mol/L) nickel ion concentrations, when the concentration of the complexing agent is very large compared with nickel concentration, do the residual nickel concentrations increase with the increase in concentration of the complexing agent. Similar results were obtained for Co(II)-glycine and Co(II)-citrate complexes.

The insignificant influence of complexing agents on oxalate precipitation in acidic solutions enables use of this precipitation for metal recovery from spent electroless nickel solutions. It is suitable only for solutions containing small amounts of phosphite (about 0.2 mol/L), however. Spent commercial electroless nickel plating solutions contain much more phosphite. For example, for solutions containing (mol/L): Ni(II) - 0.1, glycine - 0.4, phosphite - 2.2. After acidifying with sulfuric acid to pH 1.0 and oxalate precipitation, the extent of recovered metal was about 70 percent (*i.e.*, the residual metal concentration in the solution was 1.5 g/L). Much better results were obtained when phosphoric acid was used as acidifier. In this case, residual nickel concentration was 50 mg/L.

Table 3
Influence of Beginning Concentration of Metal Ion on Metal Recovery by Oxalate Precipitation

Beginning Metal Conc., mol/L		Residual Metal Conc., mg/L pH 0	pH 1	pH 2
	0.01	46	50	560
Cu(II)	0.05	18	23	1200
	0.1	13	27	640
	0.01	590	50	8
Ni(II)	0.05	26	20	46
	0.1	1	7	23
	0.01	630	50	6
Co(II)	0.05	47	20	33
	0.1	7	5	50

In solutions containing copper complexes of tartrate and EDTA at low pH, precipitation of insoluble EDTA[2] and tartrate[3] compounds takes place. Figure 2 shows a much more complicated process than oxalate precipitation. In acidic solutions, the extent of removal of tartrate and EDTA depends on their concentrations and pH and is 30 to 60 percent for tartrate and 85 to 98 percent for EDTA.

The by-products of spent electroless copper solutions containing EDTA have much less influence on oxalate precipitation than in spent electroless nickel solutions. Oxalate precipitation has the same characteristics in fresh solutions as in spent electroless copper solutions. It enables use of oxalate precipitation for recovery of both copper and EDTA for reuse in fresh plating solutions.

Oxalic acid (0.3 M) and sulfuric acid to pH 0 were added to 1-L spent electroless copper solutions containing (mol/L): Cu(II) - 0.1, EDTA - 0.15, glycine - 0.1. Copper oxalate and H_4EDTA-acid precipitates were formed:

$$\mathrm{CuEDTA^{-2} + H_2C_2O_4 + 2H^+ \rightarrow CuC_2C_4\downarrow + H_4EDTA\downarrow}$$

The precipitates were dissolved in sodium hydroxide:

$$\mathrm{CuC_2O_4 + H_4EDTA + 2NaOH \rightarrow CuEDTA^{-2} + Na_2C_2O_4\downarrow + 2H_2O.}$$

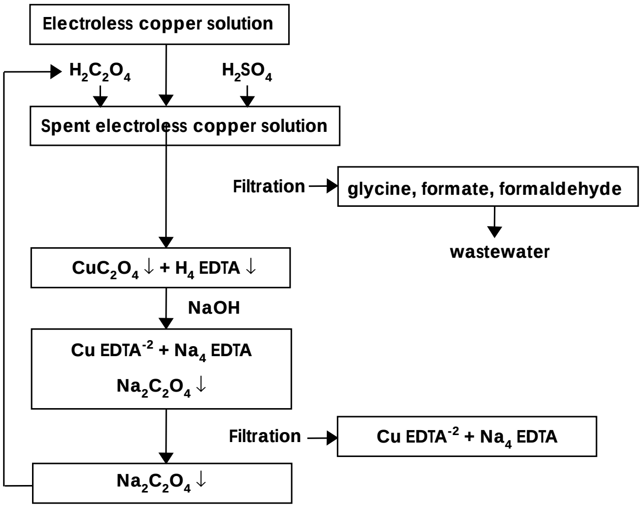

Fig. 3—Flow chart of regeneration of spent electroless copper solution.

After filtering of insoluble sodium oxalate, the solution was used for preparing a plating bath (Fig. 3). Such procedure enables recovery of 95 percent of the EDTA and 99.5 percent of the Cu(II). The presence of oxalate in electroless copper solutions does not affect the plating process.

Summary

The metals from spent electroless plating solutions can be recovered by means of pH change and addition of oxalate. For spent electroless copper plating solutions containing EDTA, oxalate precipitation can be used for recovery of both Cu(II) and EDTA at 99.5 and 95 percent, respectively.

Editor's note: Manuscript received, May 1994.

References

1. C.S. Brooks, *Metal Fin.*, **87**, 33 (May 1989).
2. H. Honma, H. Matsui, H. Kohara, *J. Metal Fin. Soc. Japan*, **27**, 195 (1976).
3. A.K. Pigaga, A.A-K. Žukauskaitė and M-G. A. Klimantavičiutė, *LTSR MA Darbai, Ser. B*, **6**(157), 50 (1986).

About the Authors

Dr. Ona Gylienė is a scientific associate in the Institute of Chemistry, Goštauto 9, Vilnius 2600, Lithuania. She is a graduate of the University of Vilnius and obtained her doctorate in electroless plating. Her research involves wasteless electroplating and she has published about 50 scientific and engineering papers.

Dr. Mudis Šalkauskas is head of Environmental Chemistry at the Lithuanian Institute of Chemistry, and is chairman of the Technical Committee (TC 16) on Chemical Analysis of the standardization body of Lithuania. He has published about 200 scientific papers, as well as several books on plating of plastics and environmental protection by means of wasteless technologies. His research interests include chemical kinetics and ecology.