

## Recovery of Nickel from Spent Electroless Nickel Plating Baths

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With increasing importance of electroless nickel plating technology in many fields such as electronic and automobile industries, the treatment of the spent baths is becoming a serious problem. These spent baths contain iron and zinc as impurities, organic acids as complexing reagents, and phosphonate ions as oxidized species of the reducing reagent, as well as several grams per liter of nickel. The spent baths are currently treated by conventional precipitation method, but a method with no sludge generation is desired. This work aims at establishing a recycling process of nickel from the spent baths using solvent extraction. Extraction behaviors of nickel, iron, and zinc in various types of real spent baths are investigated as a function of pH using LIX84I, di(2-ethylhexyl)phosphoric acid (D2EHPA), and PC88A as the extractants. Nickel is extracted by LIX84I at the equilibrium pH of more than 6 with high efficiency. For the weakly acid baths, iron and zinc are extracted by D2EHPA or PC88A without adjusting the pH of the baths leaving nickel in the aqueous phase. Stripping of nickel from LIX84I with sulfuric acid is also investigated. It is shown that concentrated nickel sulfate solution ( $> 100 \text{ kg-Ni/m}^3$ ) is obtained. This solution can be reused in the electroless plating process. Based on these findings, flow sheets for recovering nickel from the spent baths are proposed.

Keywords: Electroless nickel plating, spent bath, solvent extraction, LIX84I, nickel

### Introduction

Surface finishing technology is playing an increasingly important role in the high-tech industries. As a result of this, the compositions of the effluents from these industries have become very complicated. These effluents are now being treated by the conventional precipitation method; however, due to the limitation of the dumping site, it is necessary to develop a new method for the effluent treatment in order to reduce the amount of wastes.

Electroless nickel plating is a typical surface finishing technology indispensable in the electronic and the precision machinery industries. The baths used in the electroless nickel plating contain, in most cases, nickel sulfate (source of nickel), sodium phosphinate (reducing agent), organic acids (complexing reagent, buffer). With the repeated usage of these baths, sulfate ion, sodium ion, phosphonate ion formed by the oxidation of phosphinate ion, zinc and iron dissolved from the surface of the plating target accumulate in the baths. As a result, the baths become unstable, and plating performance is decreased. Thus, at present, the baths are disposed as spent baths and treated by the conventional precipitation method.

Therefore, from the standpoint of environmental protection and resource preservation, the development of a method for recovering nickel from these spent baths is highly desired.

Many methods such as precipitation, ion exchange, adsorption, and solvent extraction are known as separation methods for the metal ions in the aqueous solutions. Among these, solvent extraction is effective in

the mutual metal separation and advantageous to the solutions with relatively high metal concentration. Thus, solvent extraction is expected to be effective in the treatment of the spent baths containing nickel in the order of  $\text{kg/m}^3$ .

Brooks [1] proposed a solvent extraction method in order to remove the impurity metals of iron, copper, zinc, and lead in the spent electroless nickel plating baths with the mixture of LIX63 and di(2-ethylhexyl)phosphoric acid (D2EHPA). In his study, the separation of nickel from phosphonate ion was not investigated. Later, however, he presented a method to separate nickel from the extraction raffinate by the precipitation as nickel oxalate followed by the nickel removal from the filtrate by the cation exchange resin. In this method, the recovery of nickel is 95%, which is not satisfactory yet. Niinae et al. [2] investigated the applicability of the various solvent extractants by using the model solutions of spent electroless nickel baths, and reported that tri-n-octylmethyl ammonium chloride and LIX26 are effective in caustic alkaline and ammoniacal alkaline baths, respectively. However, they could not find the suitable extractants for the acidic bath.

The present authors have already found that a typical hydroxyoxime extractant [3], LIX84I, is effective in the extraction of nickel from spent electroless nickel-phosphorus alloy plating bath [4]. In the present paper, therefore, another two kinds of spent electroless nickel plating baths are subjected to the extraction experiment with LIX84I. Removal of iron and zinc as impurities before the extraction with LIX84I is also investigated. The assessment of the stripping operation in order to obtain concentrated nickel sulfate solution ( $\text{Ni} > 100 \text{ kg/m}^3$ ) is also done by the McCabe-Thiele analysis.

## Experiment

### *Spent Baths and Reagents*

Two kinds of spent baths (A and B) discharged from an electroless nickel plating plant in Japan were used for the extraction experiments. Chemicals used in this experiment were all reagent grade except for the extractants and diluent. LIX84I (Henkel), D2EHPA (Daihachi), and PC88A (Daihachi) were used as received. These were respectively dissolved in Shellsol D70 (Shell Chemicals) in order to prepare the working organic phases. The concentrations of the extractants were 20 vol% for LIX84I and 10 vol% for D2EHPA and PC88A. Various concentrations of sodium hydroxide and hydrochloric acid as well as ion exchange - distilled water were used as pH adjusting reagents.

### *Extraction, Stripping, and Analysis*

In the experiment investigating the pH dependency of the extraction, the working organic phase, spent bath, and pH adjusting reagent were poured into a stoppered conical flask at the volume ratio of 5:4:1, and shaken in a water bath maintained at  $298 \pm 0.1$  K for more than 24 hours to ensure equilibrium. After shaking, the mixture was centrifuged, and the organic phase was pipetted out.

In the experiment to obtain the extraction isotherm of zinc with PC88A, spent bath A was contacted with the organic phase without the pH adjustment at different volume ratios in the same manner as in the former experiment.

In the nickel stripping experiment, the organic phase containing  $8.77 \text{ kg/m}^3$  was first prepared by contacting the 20vol% LIX84I with  $1.00 \text{ kmol/m}^3 (\text{NH}_4)_2\text{SO}_4 - 0.1 \text{ kmol/m}^3 \text{ NiSO}_4 - 0.4 \text{ kmol/m}^3 \text{ NaOH}$  solution at the volume ratio of 1:3 in a separatory funnel at room temperature followed by washing with water. The obtained organic phase was then contacted with  $0.92 \text{ kmol/m}^3 \text{ NiSO}_4 - 1.00 \text{ kmol/m}^3 \text{ H}_2\text{SO}_4$  solution (nickel concentration was  $54.0 \text{ kg/m}^3$ ) at different volume ratios in the same manner as in the former experiment.

The metal contents in the aqueous phases after extraction and stripping were determined by ICP-AES (Seiko SPS4000). The metal contents in the organic phase after extraction and stripping were determined by ICP-AES after stripping the metals in the organic phases using an excess volume of 1-2  $\text{kmol/m}^3$  hydrochloric acid. The pH values in the aqueous phases were measured by a pH meter (Toa HM-50AT). Sulfate, phosphinate, and phosphonate ions as well as the organic acids in the spent baths were determined by a capillary electrophoresis apparatus (Otsuka CAPI-3200).

## Results and Discussion

### *Compositions of the Spent Baths*

The compositions and pH values of the spent baths were measured, and the results are shown in Table 1. For comparison, those of the spent bath C which was dealt with in our previous study [4] is also shown in this table.

Spent bath A is weakly acidic bath with low accumulation of phosphonate and sulfate ions, but contains the highest concentration of zinc.

Spent bath B is almost neutral and contains boron with a high accumulation of phosphate and sulfate ions.

Spent bath C is a typical weakly acidic bath with a high accumulation of phosphonate and sulfate ions.

Table 1 The Compositions ( $\text{kg/m}^3$ ) and pH Values of the Spent Baths A, B, and C.

	A	B	C[4]
Sodium	24	90	66
Nickel	6	6	4
Iron	0.003	0	0.1
Zinc	0.07	0.007	0.01
$\text{SO}_4^{2-}$	7	64	48
$\text{H}_2\text{PO}_2^-$	19	12	16
$\text{HPO}_3^{2-}$	17	100	98
Lactic Acid	3	8	31
Propionic Acid	0	35	2
Malic Acid	24	0	0
Succinic Acid	7	0	0
Boron	0	0.8	0
Glycine		30	
pH	4.8	6.0	4.5

### *Extraction with LIX84I*

Figures 1, 2, and 3 show the extraction percentages of nickel, iron, and zinc with LIX84I as a function of the equilibrium pH values from the spent baths A, B, and C, respectively.

In spent baths A and C, when water is used as a pH adjusting reagent; that is, the extraction was done substantially without pH adjustment, the extraction percentages of nickel are only 43% (pH 4.4) and 34% (pH 4.1), respectively. However, when the pH is increased to greater than 6, the extraction percentages of nickel are enhanced to more than 99.9% (99.97% at pH 6.1 and 99.94% at pH 6.2 for spent baths A and C, respectively). Since the extraction percentages of iron and zinc are low throughout the pH range in these experiments, it is expected to selectively extract nickel leaving most of iron and zinc in the raffinate.

In spent bath B, when the extraction is done substantially without pH adjustment, the extraction percentage is greater than 99.0% (pH 5.9). About 70% of the zinc was also extracted when the pH is greater than 5; however, the concentration of zinc in the spent bath C is so low that the coextraction of zinc would cause little problem when the recovered nickel is reused in the electroless plating process.

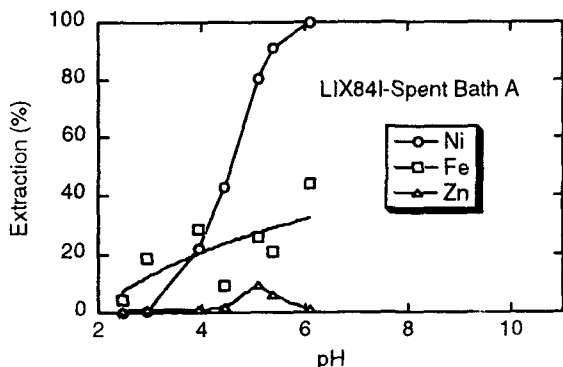


Fig. 1 The effect of equilibrium pH on the extraction of metals from spent bath A with 20vol% LIX84I dissolved in Shellsol D70 at 298K.

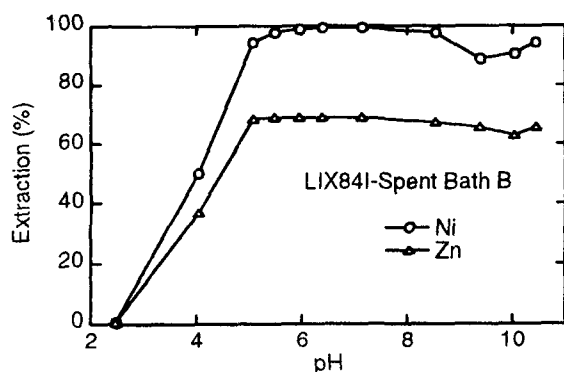


Fig. 2 The effect of equilibrium pH on the extraction of metals from spent bath B with 20vol% LIX84I dissolved in Shellsol D70 at 298K.

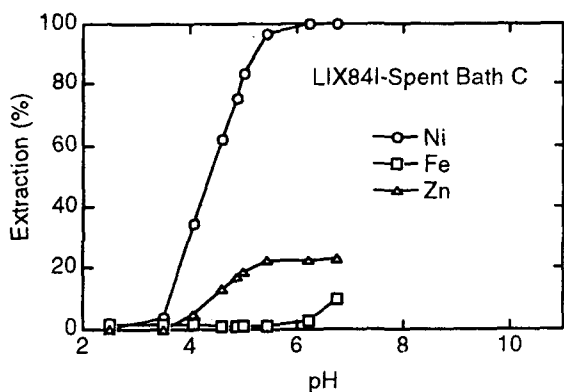


Fig. 3 The effect of equilibrium pH on the extraction of metals from spent bath C with 20vol% LIX84I dissolved in Shellsol D70 at 298K [4].

The McCabe-Thiele analysis of the nickel extraction isotherm of spent bath C at the initial pH of 6.4 reveals that when the ratio of the flow rates (aqueous to organic) is 2, the number of stages necessary to completely extract nickel by countercurrent contact is 2. By using the two-stage extraction, 4 kg/m<sup>3</sup> nickel in spent bath C would be reduced to 0.0006 kg/m<sup>3</sup> [4].

#### Extraction with D2EHPA and PC88A

In order to recover nickel with a higher purity and simplify the treatment of the aqueous raffinate after the extraction with LIX84I, the application of D2EHPA and PC88A has been investigated by using spent bath A to remove iron and zinc before extracting nickel with LIX84I.

Figures 4 and 5 present the extraction percentages of nickel, iron, and zinc as a function of the equilibrium pH values with D2EHPA and PC88A, respectively. When water is used as the pH adjusting reagent, that is, the extraction is substantially done without any pH adjustment, the extraction percentages of nickel, iron, and

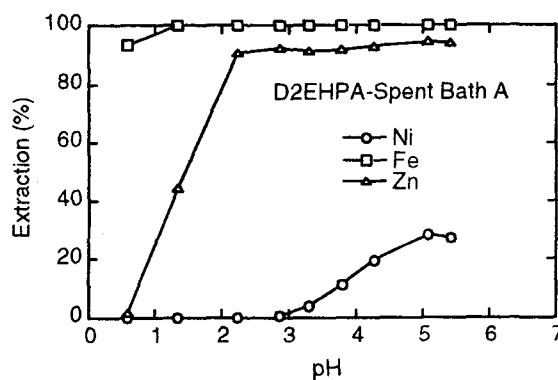


Fig. 4 The effect of equilibrium pH on the extraction of metals from spent bath A with 10vol% D2EHPA dissolved in Shellsol D70 at 298K.

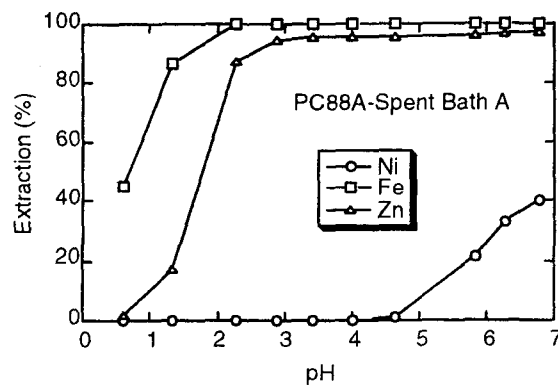


Fig. 5 The effect of equilibrium pH on the extraction of metals from spent bath A with 10vol% PC88A dissolved in Shellsol D70 at 298K.

zinc with D2EHPA were 20%, 100%, and 90%, respectively (pH 4.3), while those with PC88A were 1%, 100%, and 95% (pH 4.6). Thus, both extractants exhibit high extraction abilities for iron and zinc without pH adjustment. Since the extraction percentage of nickel with PC88A is lower than that with D2EHPA, PC88A is more suitable for the selective extraction of iron and zinc.

Figure 6 presents the extraction isotherm of zinc with PC88A. The McCabe-Thiele analysis reveals that when the ratio of the flow rates (aqueous to organic) is 5 and the feed zinc concentrations in the aqueous and organic phases are 150 g/m<sup>3</sup> and 5.6 g/m<sup>3</sup>, respectively, one stage operation can reduce the zinc concentration in the aqueous phase to 5.8 g/m<sup>3</sup> and at the same time generate the organic phase containing 757 g/m<sup>3</sup> of zinc.

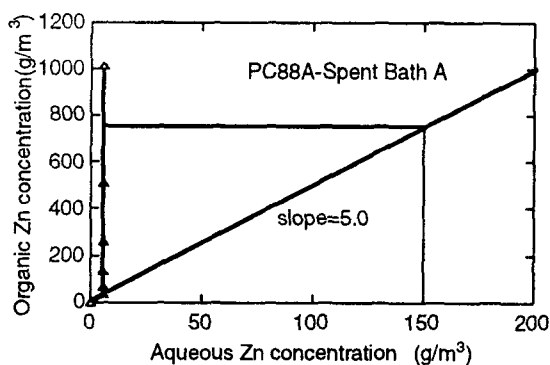
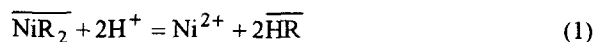


Fig. 6 Extraction isotherm of zinc with 10 vol% PC88A dissolved in Shellsol D70 from spent bath A at 298K.

#### Stripping of Nickel from LIX84I with Sulfuric Acid

In our previous study [4], the effect of pH on the nickel stripping percentage with sulfuric acid was studied at 298 K using 20vol% LIX84I dissolved in Shellsol D70 containing 9.1 kg/m<sup>3</sup> of nickel. As a result, more than 99% of the nickel was stripped at the equilibrium pH of less than 2.7 (the initial sulfuric acid concentration was greater than 0.17 kmol/m<sup>3</sup>). The concentration of nickel in the obtained aqueous phase after stripping was low, because the phase ratio in that experiment was unity. For the reuse of the recovered nickel sulfate solution as a source of nickel for the electroless nickel plating baths, the concentration of nickel should be as high as possible, and the free sulfuric acid remaining in the solution should be as low as possible.

In order to assess the operational conditions for obtaining such a solution, the stripping isotherm of nickel from nickel-loaded LIX84I was constructed using the 0.92 kmol/m<sup>3</sup> NiSO<sub>4</sub> - 1.00 kmol/m<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> solution as the stripping reagent (Fig. 7). The stoichiometric relation of the stripping of nickel from LIX84I by acid is expressed by the following equation [5].



Here, HR and the bar denote the monomer of the active component of LIX84I and the organic phase species, respectively. As seen in this equation, one nickel ion in the organic phase exchanges with two hydrogen ions in the aqueous phase during stripping. The dotted line in Fig. 7 signifies the theoretical maximum nickel concentration after stripping calculated by assuming that all of the hydrogen ions in the sulfuric acid are exchanged with the nickel ion in the organic phase when the amount of nickel in the initial organic phase stoichiometrically exceeds that of the hydrogen ion in the initial aqueous phase.

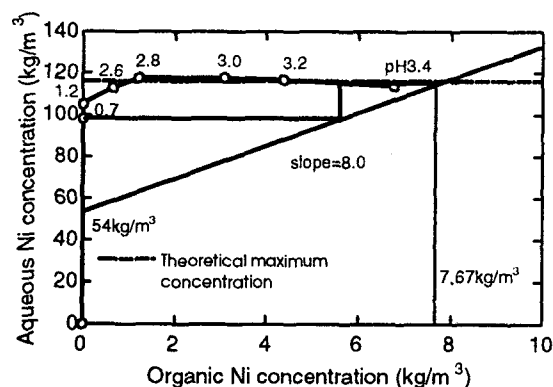


Fig. 7 Stripping isotherm of nickel from 20vol% LIX84I dissolved in Shellsol D70 containing 8.77 kg/m<sup>3</sup> of nickel with 0.92 kmol/m<sup>3</sup> NiSO<sub>4</sub>-1.00 kmol/m<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> solution at 298K.

According to the experimental results, with the increasing nickel concentration in the organic phase, the nickel concentration in the aqueous phase is enhanced, reaches the theoretical maximum value (117 kg/m<sup>3</sup>) when the nickel concentration in the organic phase is 1.21 kg/m<sup>3</sup>, and remains almost constant thereafter. The pH value continues to increase after the nickel concentration in the aqueous phase becomes almost constant and seems to approach 4.99, which is the pH value of the 1.92 kmol/m<sup>3</sup> nickel sulfate solution (117 kg-Ni/m<sup>3</sup>). This suggests that a small amount of hydrogen ion in the aqueous phase is exchanging with nickel in the organic phase even after the nickel concentration in the organic phase becomes almost constant.

The McCabe-Thiele analysis reveals that when the ratio of the flow rates (organic to aqueous) is 8 and the nickel concentration in the feed organic phase is 7.67 kg/m<sup>3</sup>, two stage countercurrent contact can reduce the nickel concentration in the organic phase to a trace level and concentrate the nickel in the aqueous phase from 54 kg/m<sup>3</sup> to 117 kg/m<sup>3</sup>.

As shown here, it is possible to obtain concentrated nickel sulfate solution (nickel concentration  $> 100 \text{ kg/m}^3$ ) at pH 3.3. The impurity contents in this solution would be sufficiently low and thus can be used as a nickel source for the electroless nickel plating process.

#### Proposed Flow Sheets for the Recovery of Nickel from Spent Bath

Based on the experimental results obtained in this study, the flow sheet for the recovery of nickel from spent bath A is proposed in Fig. 8. Initially, zinc and iron are removed with PC88A without the pH adjustment. Then, nickel is extracted with LIX84I at the equilibrium pH of 6-7 by adding alkaline to the raffinate. The extracted nickel is stripped with the mixed solution of  $1 \text{ kmol/m}^3$  sulfuric acid and nickel sulfate containing  $50 \text{ kg/m}^3$  nickel in order to obtain the concentrated nickel sulfate solution of high purity, which would be reused in the electroless nickel plating process. This flow sheet would also be applied to spent bath C because of the similarity in pH. For spent bath B, nickel is extracted with LIX84I without the pH adjustment and stripped by the same way as that for spent bath A.

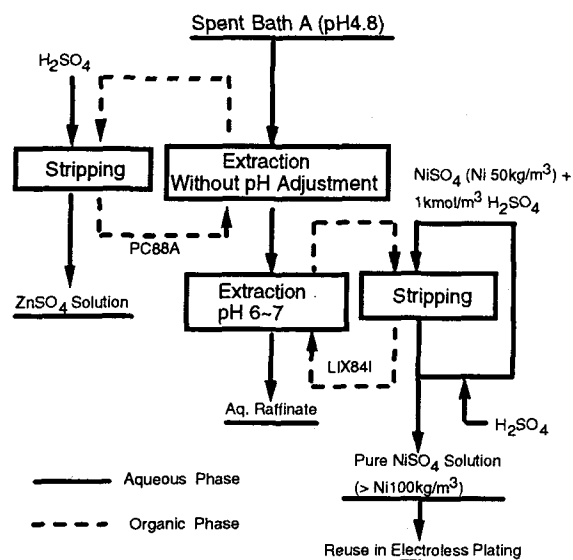


Fig. 8 Proposed flowsheet for the recovery of nickel from spent bath A.

#### Conclusions

LIX84I is capable of extracting nickel from spent electroless nickel plating baths with good selectivity at pH values greater than 6.

Iron and zinc as impurities in the spent baths can be removed with an organophosphorus acid extractant such as D2EHPA and PC88A before the nickel extraction with LIX84I. The pH adjustment is not necessary in this case. PC88A is more suitable for this purpose than D2EHPA

because the coextraction of nickel is lower. This process will simplify the treatment of the raffinate after nickel extraction and will contribute to produce higher purity nickel sulfate.

Nickel extracted by LIX84I can be stripped with  $1 \text{ kmol/m}^3$  sulfuric acid solution. When nickel sulfate ( $50 \text{ kg/m}^3$  nickel) is added to the stripping reagent, it is possible to obtain a concentrated nickel sulfate solution ( $> 100 \text{ kg-Ni/m}^3$ ) containing a very low amount of free sulfuric acid by countercurrent contact with 2 stages. This nickel sulfate solution would be reused in the electroless nickel plating process.

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