

Recycling of Nickel from Spent Electroless Nickel Plating Baths Using Solvent Extraction

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With increasing importance of the electroless nickel plating technology in many fields such as electronic and automobile industries, the treatment of the spent baths is becoming a serious problem. The spent baths are currently treated by the conventional precipitation method, and nickel in these baths is not recycled. Therefore, a method to recycle nickel without sludge generation should be developed. This paper outlines our attempt to establish a recycle process of nickel in the spent baths from electroless nickel plating plants using solvent extraction. Nickel in the actual spent baths is efficiently extracted by a hydroxyoxime extractant such as LIX84I at a pH greater than 6 and is readily stripped with sulfuric acid. The application of acidic organophosphorus extractants to selectively remove impurity metal ions (iron and zinc) from actual spent baths before extracting nickel leads to the finding that PC88A and Cyanex272 effectively remove iron and zinc without pH adjustment leaving nickel in the raffinate. Based on these results, a flowsheet for the recycling nickel from the spent baths has been proposed.

Key words: electroless nickel plating, solvent extraction, recycling, LIX84I, acidic organophosphorus extractants

1. INTRODUCTION

Electroless nickel plating is now one of the most important surface finishing technologies in high-tech industries. As a result, the treatment of the spent baths and waste rinse water in the electroless nickel plating plants is becoming a serious problem. The annual discharge of the spent baths amounts to 0.12 million ton in Japan.

These waste solutions contain iron and zinc as impurities, organic acids as complexing reagents, and phosphonate ions as the oxidized species of the reducing reagent, and are currently treated by a conventional precipitation method; however, a method with no sludge generation is 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 kg/m^3 .

We are studying the recycling process of nickel in the spent baths by using solvent extraction, and this paper outlines some of these results.

2. EXPERIMENTAL

2.1 Spent Baths and Reagents

The spent baths discharged from an electroless nickel plating plant in Japan were used for the extraction experiments. Typical examples of the compositions of the spent baths are shown in Table 1. Chemicals used in this experiment were all reagent grade except for the extractants and diluent.

Table 1 Compositions (kg/m^3) and pH of the spent baths.

	A	B	C
Sodium	66	24	68
Nickel	4	6	4
Iron	0.1	0.003	0.09
Zinc	0.01	0.07	0.008
SO_4^{2-}	50	7	41
H_2PO_2^-	16	19	15
HPO_3^{2-}	98	17	80
Lactic Acid	30	3	35
Propionic Acid	2	0	4
Malic Acid	0	24	0
Succinic Acid	0	7	0
pH	4.5	4.8	4.6

LIX84I (active component: 2-hydroxy-5-nonylaceto-phenone oxime, Cognis), LIX63 (8-methyl-7-hydroxydodecane-6-oxime, Cognis), D2EHPA (bis(2-ethylhexyl)phosphoric acid, Daihachi), PC88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, Daihachi), and Cyanex272 (bis(2, 4, 4-trimethylpentyl)phosphinic acid, Cytec) were used as extractants without further purification. 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, PC88A, and Cyanex272. Various concentrations of sodium hydroxide and hydrochloric acid as well as ion exchange – distilled water were used as pH adjusting reagents.

2.2 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 ± 0.1 K overnight to ensure equilibrium. After shaking, the mixture was centrifuged, and the organic phase was pipetted out. 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 kmol/m³ hydrochloric acid. The pH values in the aqueous phases were measured by a pH meter. 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).

3. RESULTS AND DISCUSSION

3.1 Extraction and Stripping of Nickel

Based on the screening tests, LIX84I, a typical chelating reagent, has been selected as an effective extractant of nickel in the spent baths. Figure 1 shows the effect of the equilibrium pH on the extraction percentage of each metal ion from the spent bath A by using LIX84I. According to this figure, the extraction percentage of nickel is only 35% without the pH adjustment (equilibrium pH is about 4), but markedly increases to more than 99% under the pH greater than 6. In this case, the extraction percentages of iron and zinc are so low that nickel can be extracted selectively [1].

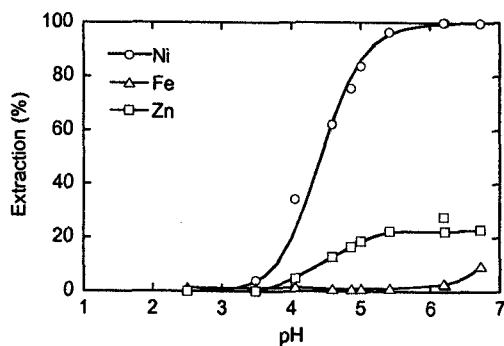


Figure 1 Extraction of the metal ions from the spent bath A with 20 vol% LIX84I as a function of the equilibrium pH.

Extraction isotherm of nickel when the initial pH was 6.4 was constructed and analyzed. The result revealed that when the ratio of the flow rates (aqueous to organic) is 2, the number of stages necessary to completely extract the nickel by countercurrent contact is 2. By using the two-stage extraction, 4 kg/m³ nickel would be reduced to less than 1 g/m³ [1].

The effect of pH on the nickel stripping percentage from the nickel-loaded organic phase using various concentrations of sulfuric acid was studied at 298 K using LIX84I containing 9.1 kg/m³ of nickel at the phase ratio of unity. The result showed that more than 99% of the nickel is stripped at the equilibrium pH of less than 2.7 (the

initial sulfuric acid concentration was greater than 0.17 kmol/m³) [1].

In order to reuse 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. From this viewpoint, the nickel stripping isotherm from the LIX84I containing 8.8 kg/m³ of nickel was obtained using the mixed solution of 0.92 kmol/m³ NiSO₄ and 1.00 kmol/m³ H₂SO₄. According to the McCabe-Thiele analysis, when the ratio of the flow rates (organic to aqueous) is 8 and the nickel concentration in the feed organic phase is 7.7 kg/m³, the nickel concentration in the organic phase can be reduced to a trace level, and simultaneously, the nickel concentration in the aqueous phase can be increased from 54 kg/m³ to 117 kg/m³ [2].

If the pH adjustment is unnecessary, the recycling process would become more advantageous from the economical viewpoint. We found that the mixture of LIX63 and the acidic organophosphorous extractant such as D2EHPA and PC88A enhances the equilibrium extraction of nickel from the spent bath. For example, the mixture of LIX63 (20 vol%) and D2EHPA (20 vol%) extracts nickel with an efficiency of more than 95% without pH adjustment as shown in Fig. 2. However, it becomes difficult to completely strip the extracted nickel using a moderate concentration of sulfuric acid as shown in Fig. 3 [3].

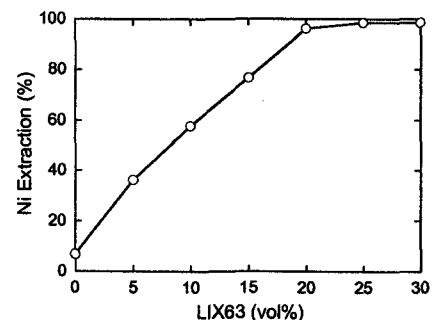


Figure 2 Effect of the LIX63 concentration on the extraction of nickel from the spent bath C with the mixture of 20 vol%D2EHPA and LIX63.

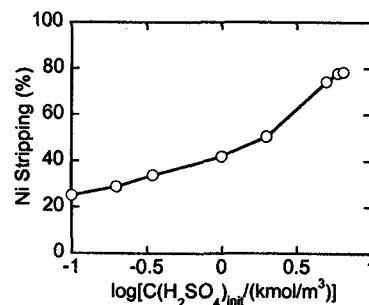


Figure 3 Effect of the initial sulfuric acid concentration on the stripping of nickel from the mixture of 20 vol%D2EHPA and 20%LIX63. Initial nickel concentration was 7.2 kg/m³.

3.2 Removal of Impurity Metal Ions

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 acidic organophosphorus extractants such as D2EHPA, PC88A, and Cyanex272 has been investigated using the spent bath B to remove iron and zinc before extracting nickel with LIX84I.

Figure 4 shows the extraction percentages of nickel, iron, and zinc as a function of the equilibrium pH values with PC88A [2]. Similar experiments were also conducted using D2EHPA and Cyanex272. All the extractants exhibit high extraction abilities for iron and zinc without pH adjustment. Since the extraction percentages of nickel with PC88A and Cyanex272 are much lower than that with D2EHPA, PC88A and Cyanex272 are more suitable for the selective extraction of iron and zinc.

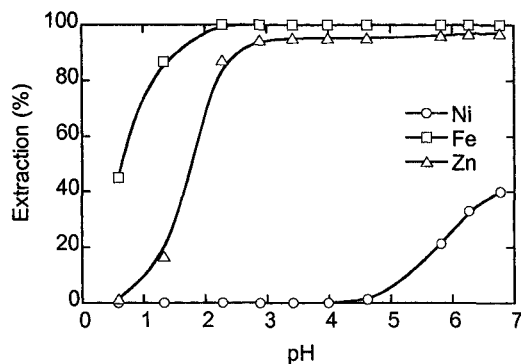


Figure 4 Extraction of the metal ions from the spent bath B with 10 vol%PC88A as a function of the equilibrium pH.

Application of solvent impregnated resin or fiber would be also effective to remove impurities. In particular, solvent impregnated fiber using oil sorbent as support showed the advantage over solvent extraction and solvent impregnated resin in terms of the amount of extractant necessary to achieve a certain removal percentage and over solvent impregnated resin in terms of removal rate [4].

4. CONCLUSIONS

Based on the experimental results obtained in this study, the flow sheet for the recovery of nickel from the spent baths is proposed as shown in Fig. 5 [2]. 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 kmol/m³ sulfuric acid and nickel sulfate containing 50 kg/m³ nickel in order to obtain the concentrated nickel sulfate solution of high purity, which would be reused in the electroless nickel plating process.

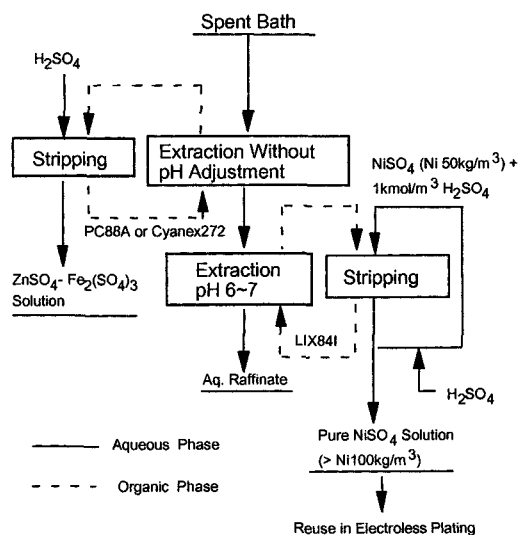


Figure 5 Proposed flowsheet for the recovery of nickel.

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