Nickel Extraction from Waste Etching Liquor from Electronic Lead Frame Manufacturing

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Abstract

Acidic concentrated ferric chloride solution is used as an etching solution in the etching process during the manufacture of electronic lead frames. After etching, there are several metal contaminates in the waste etching solution. Nickel is the main contaminant. Precipitation is currently used to remove Ni in order to recycle the etching solution. Since Ni can not be removed completely by precipitation, the etching efficiency decreases with Ni accumulation. In this work, the recovery of Ni from used etching solution by solvent extraction with 2-ethylhexanal oxime (EHO) was investigated in order to establish the new recycling process for the etching solution. It was found that with solvent extraction alone, Ni and Cu recovery were 77.8 % and 93.6 % respectively, with 1.5 M EHO and 30 min extraction time. With precipitation and solvent extraction, Ni and Cu were extracted nearly 100 % with 0.3 M EHO. Complete extraction can be obtained with 2 stage countercurrent extraction.

Introduction

The application of solvent extraction to the treatment of industrial wastes has been studied worldwide. Solvent extraction can be used to recover, reuse, and remove some metals from industrial waste solutions to preserve the environment. Fe-Ni alloy is used for lead frame material in electronic industries. In the etching process, acidic concentrated ferric chloride solution is used as an etching liquor. Etching solution consists of $FeCl_3$ 365-620 g/l [Fe(III) 125.7-213.5 g/l], HCl 1.78-2.00 mol/l, wetting agent and defoaming agent[1]. The efficiency of the etching solution is decreased due to nickel and other metals dissolved into the solution. In the current process the used etching liquor containing Ni is treated by a precipitation method[1]. The precipitated Ni is recovered and used for stainless steels. The treated etching solution is recycled to the etching process. However there is nickel residue in the range of 300-500 mg/l in treated solution. Some fresh etching solution is added in order to keep the efficiency. The current process is shown in Fig.1.

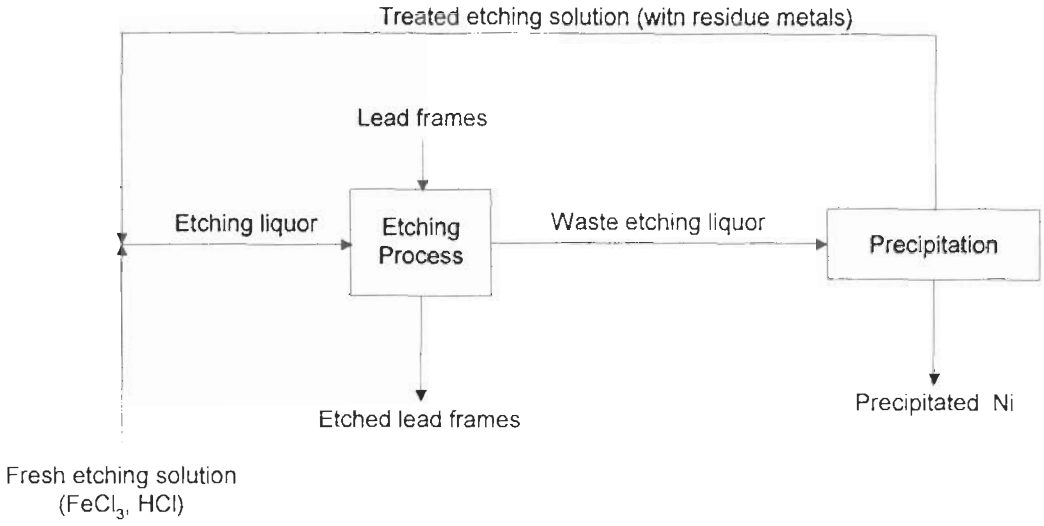


Fig. 1 The current process of used etching solution treatment.

Nickel extraction from acidic chloride solutions with 2-ethylhexanal oxime (called EHO) was studied by several investigators [2-6]. EHO can extract Ni prior to Fe[6]. Therefore, in this study Ni extraction from used etching solutions was obtained with EHO in order to establish a new recycle process for etching solution.

Experimental

Waste etching solutions analysis

The waste aqueous solutions were actual waste etching liquors from Rasa Industries, Ltd., Osaka plant, Japan. Fig. 2 shows sources of the solutions used in this study. F-1 was the waste etching solution from the etching process. F-2 was the solution after precipitation process. F-2′ was F-2 with a small amount of HCl in order to adjust pH. The concentrations of Fe, Ni, Cr, Cu, Mn, and Zn of solutions were measured by atomic absorption spectrophotometry. The Fe(II) concentration was obtained by oxidation-reduction titration with 0.25 M Ce(IV) standard solution. The Fe (III) concentration was calculated by the difference between total Fe and Fe (II). The chloride ion concentration was measured by titration with 0.1 M $AgNO_3$.

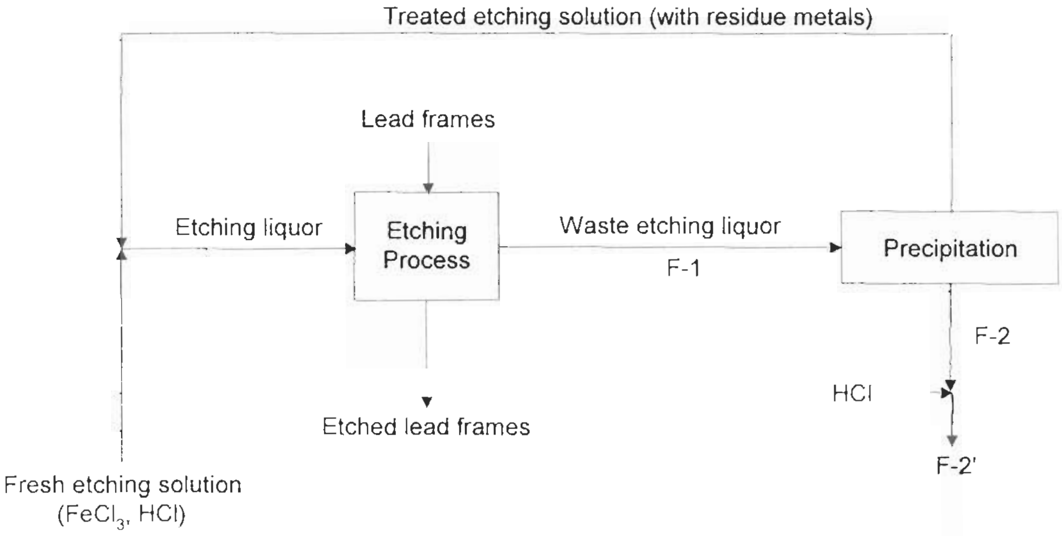


Fig.2 Sources of the aqueous solutions.

Solvent extraction

An extractant, EHO (2-ethylhexanal oxime) diluted in kerosene was used as the organic phase. The extraction experiments were investigated by placing equal volumes of the aqueous phase and the organic phase into a 50 ml centrifuge tube and shaking at 298 K and 300 spm for a specified time. After that the tube was centrifuged for 15 min to separate the two phases. The aqueous solution was analyzed for the metal concentration by atomic absorption spectrophotometry. Concentrations of Fe(III) and Fe(II) were obtained as mentioned before.

Extraction isotherm

The extraction isotherm for F-2′ was determined by contacting the organic and aqueous solutions to equilibrium at various O/A ratios, namely 1/2, 1/1.5, 1/1, 1.5/1, 2/1, 2.5/1, 3/1, 4/1, and 5/1. At each ratio, 0.3 M EHO diluted in kerosene was used as the organic phase. The experimental procedure for measuring the extraction isotherm was similar to that of solvent extraction mentioned before. The Ni concentration in the organic phase was calculated from initial and equilibrium Ni concentrations in the aqueous phase.

Results and Discussions

1. Compositions of aqueous solutions

Table 1 shows the compositions of three aqueous solutions. F-1 and F-2 were actual solutions from Rasa Industries, Ltd. F-1 solution contained a very high amount of Ni. Even after the precipitation process, F-2 still contained Ni.

During the extraction experiment of F-2, a red-brown solid, probably $Fe(OH)_3$ precipitated in the aqueous phase[7]. HCl was added to F-2 in order to adjust pH to prevent the solid precipitation. The F-2 solution with HCl added will be referred to F-2′. The F-2′ was analyzed for compositions as shown in Table 1.

Table 1
Compositions of aqueous solutions, F-1: Waste etching solution
F-2: Waste precipitation solution, F-2′: F-2 with added 2 M HCl

	F-1	**F-2**	**F-2′**	**[Unit]**
Fe(III, II)	153000	216000	189000	ppm(mg/l)
Fe(III)	103200	29000	19000	ppm
Fe(II)	49800	187000	170000	ppm
Ni	18500	2140	1900	ppm
Cr	4000	120	110	ppm
Cu	2550	4.2	3.1	ppm
Mn	646	945	831	ppm
Zn	21	17.4	13.2	ppm
Cl	8.32	7.8	8.1	mol/dm^3
pH	-0.8	1.8	0	-

2. Extraction of F-1

Table 2 shows the extraction result of metals from F-1 with 0.5M, 1.0M, and 1.5M EHO. The organic to aqueous ratio (O/A) was 1. Extraction times were 15 and 30 min. It was found that at 30 min time, extractions of Ni are 17.6, 38.4, and 77.8% and those of Cu are 48.9, 79.1, and 93.6% for 0.5M, 1.0M, and 1.5M EHO, respectively. At 15 min extraction time, the extractions of Ni and Cu are less. Fe, Mn, and Zn were not extracted by EHO. Cr was slightly extracted.

Table 2
Extraction of metals from F-1 with EHO
Conditions: Organic phase: 0.5, 1.0, and 1.5 M EHO diluted in kerosene, Aqueous phase: F-1, O/A = 1, 298 K

	Extraction [%]					
	0.5M EHO		1.0M EHO		1.5M EHO	
	15min.	30min.	15min.	30min.	15min.	30min.
Fe	-	-	-	-	-	-
Ni	12.5	17.6	31.1	38.4	64.3	77.8
Cr	-	-	-	-	7.8	9.2
Cu	45.0	48.9	76.6	79.1	90.0	93.6
Mn	-	-	-	-	-	-
Zn	-	-	-	-	-	-

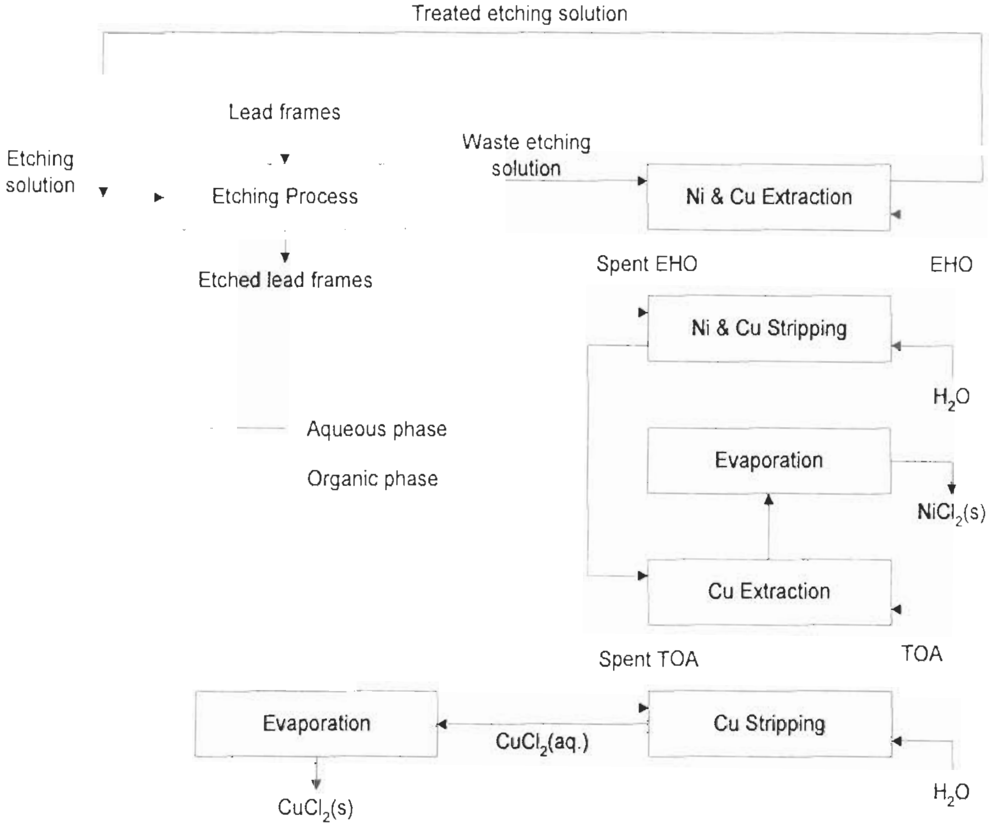


Fig. 3 First alternative for Ni and Cu Extraction

The results show that increased extraction of Ni and Cu can be achieved by using 1.5M EHO with 1-stage extraction. Multistage extraction is expected to further increase Ni and Cu extraction. Both Ni and Cu are extracted to the organic phase. There are 2 possibilities for implementation as follow.

2.1 The Co-extraction of Ni and Cu with EHO is used to remove those metals from waste etching solution as shown in Fig. 3. The raffinate aqueous solution will be recycled to the etching process while the organic phase containing Ni and Cu will be stripped with water to form Ni-Cu solution. Then the Cu can be recovered with TOA (tri-octyl amine). The raffinate containning $NiCl_2$ can be evaporated to form $NiCl_2$ salt. The spent organic TOA can be stripped to obtain $CuCl_2$ salt.

2.2 The Cu is extracted using LIX 860 (a mixture of water insoluble 5-dodecylsalicylaldoxime in 2-hydroxy-5-nonylacetophenone oxime and a high-flash point kerosene) from the waste etching solution as shown in Fig. 4. The Cu in the organic phase can be stripped with 2-3 M H_2SO_4 to obtain $CuSO_4$ solution. Ni in the raffinate from extraction with LIX 860 can be extracted with EHO. The extracted etching solution can be recycled.

Further study is needed to compare the outcome of the proposed processes with the current precipitation process.

3. *Extraction of F-2 and F-2′*

The extraction results of F-2 solution with EHO are not shown here due to precipitation of a red-brown solid (believed to be $Fe(OH_3)$) during the experiment. Precipitation causes pH of F-2 to change[7]. When the pH changes, the metal extraction also changes[2, 3, 6]. To prevent the precipitation a small amount of HCl was added to F-2 to obtain F-2′ with pH = 0 as shown in Table 1. The experimental results of solvent extraction of F-2′ without any precipitation are shown in Table 3. It can be seen that Ni and Cu extraction results are about 100% for 0.3, 0.5, and 1.0M EHO concentrations at 60 min extraction time. The 2 methods to implement solvent extraction to separate Ni and Cu mentioned above can be applied to F-2′ waste etching solution.

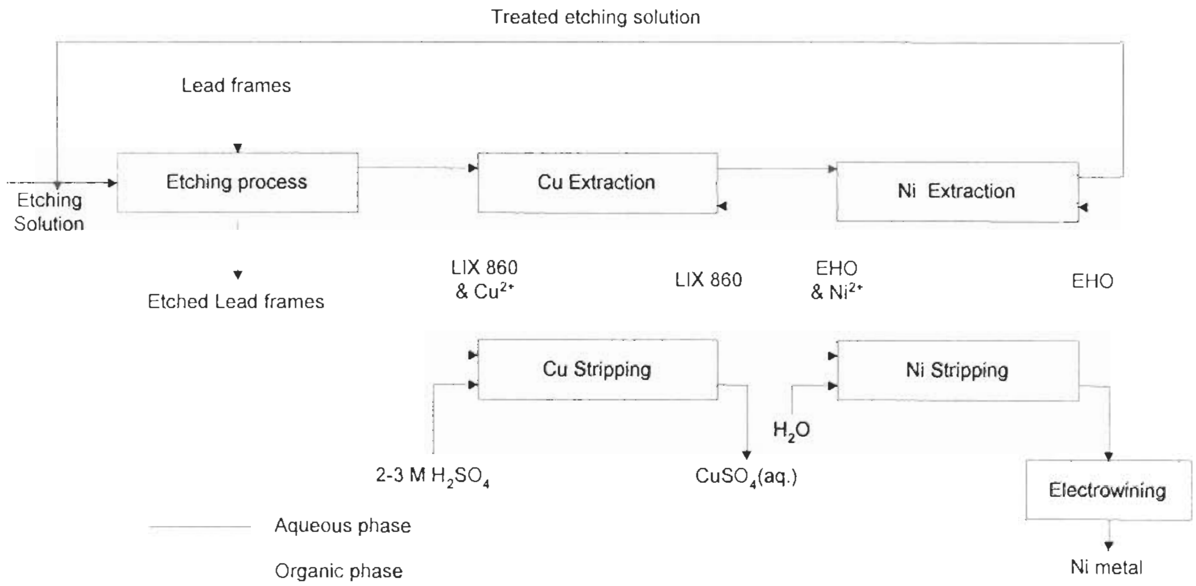


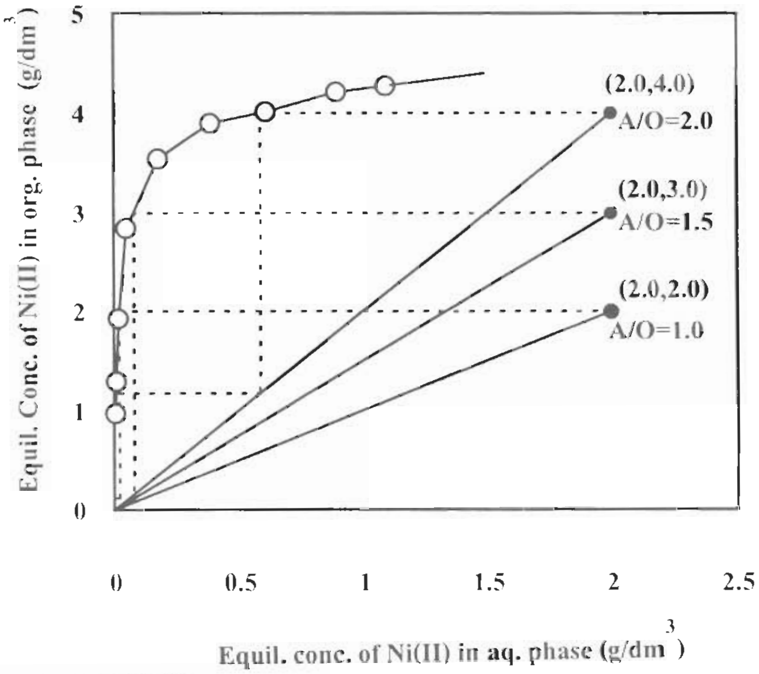
Fig.4 Second alternative for Ni and Cu extraction

Table 3
Extraction of metals from F-2′ with EHO
Conditions: Organic phase: 0.3, 0.5, and 1.0 M EHO diluted in kerosene Aqueous phase: F-2′, O/A = 1, 298 K

	Extraction [%]					
	0.3M EHO		0.5M EHO		1.0M EHO	
	30 min.	60 min.	30 min.	60 min.	30 min.	60 min.
Fe	-	-	-	-	-	-
Ni	98.6	100	99.5	99.5	99.8	99.8
Cr	-	-	-	-	-	-
Cu	91.0	98.4	100	100	100	100
Mn	-	-	-	-	-	-
Zn	-	-	-	-	-	-

4. *Extraction Isotherm of F-2′*

The extraction isotherm of Ni with 0.3M EHO for F-2′ was investigated and is shown in Fig.5. The maximum extraction of Ni is 4.4 g/dm^3 (0.075 M) with the organic phase containing 0.3M EHO. The ratio of the stoichiometric combination (concentration) of EHO and Ni in organic phase can be calculated from the maximum extraction. We obtained that the ratio of $[EHO]_{org}/[Ni]_{org}$ is 4. It means that 4 moles of EHO are needed to extract 1 mole of Ni. When the Ni concentration in waste etching solution is 2.0 g/dm^3 and Ni recovery is completed, the operating lines which the aqueous to organic phase ratio (A/O) of 1.0, 1.5, and 2.0 were drawn as shown in Fig.5. The perfect extraction of Ni from the F-2′ waste lead frame etching solution can be reached with 2 stage countercurrent extraction with 0.3M EHO. For 2 stage extraction, the aqueous phase flows countercurrent with the organic phase. In stage 1, the aqueous solution contacts with organic phase coming from second stage. After that, the aqueous from stage 1 will enter stage 2 and contact with the fresh organic phase.



Extraction condition :
Organic phase : 0.3M EHO
Aqueous phase : F-2'
O/A=1/2, 1/1.5, 1/1, 2/1, 2.5/1, 3/1, 4/1, and 5/1
298 K, 120 min

Fig. 5 Extraction isotherm

Conclusions

Extraction of Ni, Cu, and other metals with EHO was studied to obtain a new recycle process for the waste etching solution from the etching process. The results showed that Ni and Cu were extracted by EHO prior to Fe. Ni and Cu in waste etching solution straight after the etching process (F-1) were removed 77.8 % and 93.6 % respectively, with 1.5 M EHO and 30 min extraction time. Multi-stage extraction is needed for increased extraction.

Ni and Cu in waste etching solution after precipitation process with added acid to adjust pH (F-2′) were extracted nearly 100 % with 0.3 M EHO. The maximum extraction of Ni was 4.4 g/dm^3 for organic phase containing 0.3 M EHO. Complete extraction of Ni from F-2′ waste solution can be reached with 2 stage countercurrent extraction.

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