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Recovery of Nitric Acid and Valuable Metals from Spent Nitric Etching Solutions of Printed Circuit Board

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A study has been made on the recovery of nitric acid and valuable metals such as Cu, Sn, Pb from the spent nitric etching solutions. The nitric acid was extracted effectively by TBP but the heavy metals such as Fe, Cu, Sn, Pb were not extracted by TBP from the spent nitric etching solutions. From the experimental results, 95% of nitric acid in spent etching solution was extracted at O:A ratio of 3:1 with five stage by 60% TBP and 98% of nitric acid was stripped from the loaded organic phase at O:A ratio of 1:1 with four stages by distilled water. After extracting nitric acid, Cu was recovered as a metal by electrowinning effectively and Sn was successfully removed by precipitation method by adjusting the pH of raffinate solution. Finally, Pb was recovered by cementation with iron scrap at 65℃. Parameters controlling the cementation process such as temperature, pH and the effect of the additives were investigated.

Keywords: Nitric acid, recycling, extraction, recovery, etching solution.

Introduction

The spent nitric etching solutions is produced in the etching process of Printed circuited board (PCB). It containing nitric acid and the large amount of heavy metals such as copper, tin and lead. So it is regulated as specified waste in Korea[1]. Because of NOx gas production when it was incinerated after neutralizing by NaOH in Waste Treatment Company, it was a cause of environment problems. The recycle of incineration residue of complex-metal sludge is hard and these residues are buried in the ground. Therefore, the valuable metals in residue are discarded and may give rise to contamination of soil. Recoveries of nitric acid as well as valuable metals are very important to prevent the environment pollution and recycle valuable metals. Treatment methods of spent etching solutions, such as cementation [2], distillation, ion exchange [3], solvent extraction [4,5], electrowinning[6] and eletrodialysis are being studied. But these methods are only recovering nitric acid and cannot recover valuable metals from the etching solutions

In this study, the method and conditions of separation and recovery of nitric acid and valuable metals, such as copper, tin and lead from PCB etching solutions has been investigated by employing solvent extraction, electro-winning, precipitation and cementation.

Experiment

The chemical composition of synthetic spent nitric etching solutions is shown in Table 1.Separation of nitric acid from spent nitric etching solutions was extracted by TBP distilled in kerosene. Equal volumes of organic and the etching solutions were placed in a separatory funnel and shaken mechanically for 30 minutes at 25℃.

Table 1. Chemical composition of spent solder stripper

Element	Cu	Pb	Sn	Fe	HNO_3
Concentration (g/l)	33.5	40.1	44.5	21.4	3.5～4.5 N

solution.

The aqueous phase was separated after settling the mixture for 24 hours. The concentrations of nitric acid in aqueous phase were measured by titration with 0.1N NaOH and the concentrations of nitric acid in organic phase were calculated by using mass balance for nitric acid. The concentration of Cu, Fe, Sn, and Pb were measured by ICP-AES (Thermo Jarrell ash, Model Polyscan 61E). Stripping of nitric acid from organic phase was performed by distilled water with the same procedure of extraction experiment. Electrowinning experiments were carried out in a 0.5 ℓ vessel using platinized titanium cathode and a stainless steel plate as an anode. The solutions of which nitric acid was removed by solvent extraction was treated by electrowinning method. The current of electrowinning cell was controlled by a D.C. power supply (HP E3610) at constant temperature. The concentration of nitrate ion was measured by pH/ISE meter (Orion 720A). Recovery of Sn from the solutions by precitation with $Ca(OH)_2$ and

$Pb(OH)_2$ as a neutralizing agent has been performed. The precipitator was separated by decantation and Sn oxide was prepared by calcinations at 120℃ two hours.
Cementation with iron powder (99.9%, -100mesh) at 400 rpm and 80℃ were performed to recover Pb from the solutions that nitric acid, Cu and Sn were removed. Baffles were employed in the reaction vessel for

improving the stirring effect and condenser was also employed for preventing the evaporation of the solutions. The lead metal was recovered by filtering and drying from cemented Pb powder.

Results and Discussion

Recovery of nitric acid by solvent extraction

The results of extracting nitric acid from synthetic solution by TBP at O/A ratio equal to 1 are shown in Fig.1. The extraction percent of nitric acid increased with the concentration of TBP. The results of continuous batch extraction experiments at O/A ratio equal to 1 are shown in Fig.2. It is known from Fig. 2 that nitric acid (initial concentration 250g/l) was extracted 65% by 4 extraction stage at O/A=1. McCabe-Thiele diagram in the case of extracting 250g/l nitric acid by 50% TBP is shown in Fig.3.

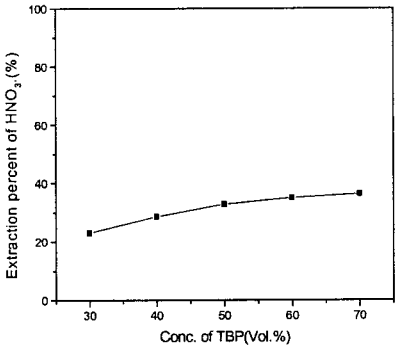

Fig. 1. Effect of concentration of extractant in the extraction of HNO_3. (O/A=1, 25℃, 4.0N HNO_3)

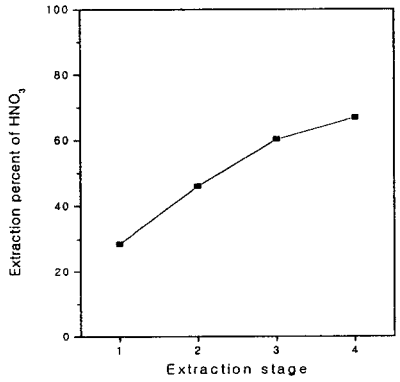

Fig. 2. Extraction percent of HNO3 at each stage.(O/A=1, 25℃, 50%TBP)

The effect of nitric acid concentration on the extraction behavior of Cu, Fe, Pb and Sn ions in mixed solution of Cu 30g/l, Pb 40g/l, Sn 40g/l and Fe 20g/l by 50% TBP was shown in Fig.4. It is known from Fig. 4 that the extraction percentage of iron increased with the concentration of nitric acid but the extraction percentage of lead and tin decreased with the increase of nitric acid concentration. The extraction percentage of copper was constant with the nitric acid concentration. From these experimental results, it is believed that TBP has selectivity for nitric acid over metal ions in the experimental ranges. Therefore, we could recover nitric acid by solvent extraction with TBP as long as the concentration of nitric acid was maintained over 0.1N.

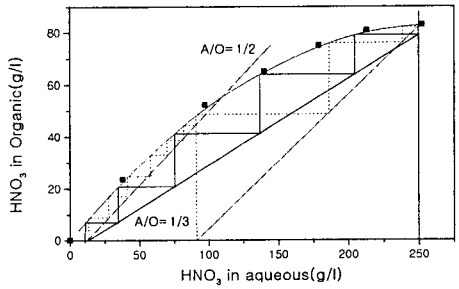

Fig. 3. McCabe-Thiele Diagram of HNO3 extracted by TBP. (25℃, 50%TBP)

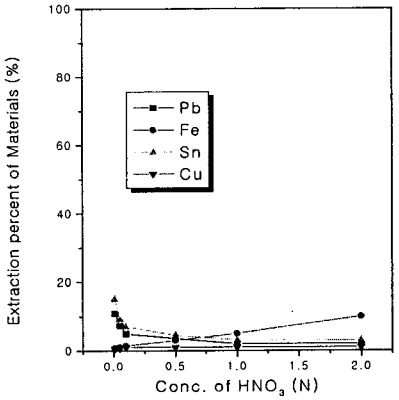

Fig. 4. Effect of HNO3 on the extraction of metal ions.(O/A=1, 25℃, 50%TBP)

The effect of TBP concentration on the recovery of nitric acid from real nitric acid spent etching solutions produced at PCB Company were investigated and the results are shown in Fig.5. The extraction percent of nitric acid by TBP increased with TBP concentration. The results of continuous batch extraction by 60% TBP are shown in Fig.6.

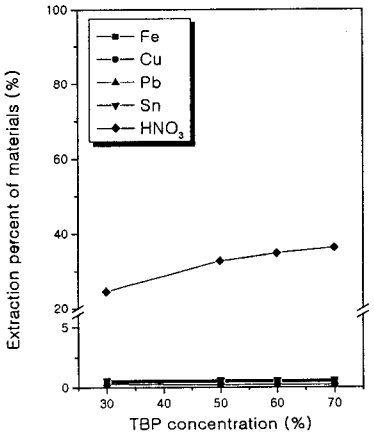

Fig. 5. Effect of TBP concentration on the extraction of metal ions. (O/A=1, 25℃, 4.0N HNO_3)

The extraction of nitric acid and metal ions were similar to the results of synthetic solution. Ninety five percent of nitric acid from initial spent etching solution was extracted by 5 extraction stage with 50% TBP but 9 extraction

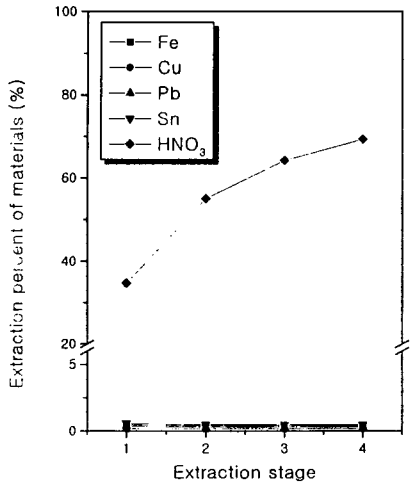

Fig. 6. Extraction percent of metal ions after each stage. (O/A=1, 25℃, 60%TBP, 4.0N HNO3)

stage was needed for the extraction of 95% nitric acid in case of O/A=2. It is known that nitric acid could be extracted by TBP as a extractant selectively in 4 extraction stage without extraction of Fe, Sn, Cu and Pb. The McCabe-Thiele diagram of nitric acid stripping by distilled water is shown in Fig.7. All of the nitric acid in the organic phase in which the concentration of nitric acid was 80g/l was stripped in 4 stripping stage at O/A=2.

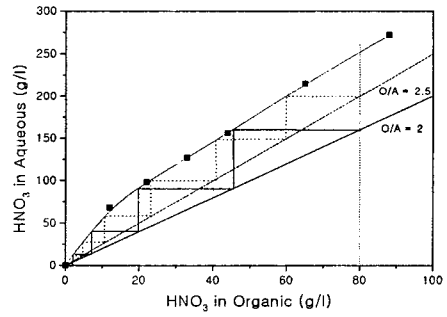

Fig. 7. McCabe-Thiele Diagram of HNO_3 stripped by water. (25℃)

Recovery of Cu by electrowinning

Because of high acid concentration in spent etching solution, metal ions in solutions could not be electrodeposited. Therefore, electrowinning experiment from the solution has been performed after decreasing the concentration of nitric acid by solvent extraction with TBP. The results of electrowinning is shown in Fig.8 at 3.0A and 1.9N nitric acid. The concentration of Cu decreased rapidly from 14.2g/l to 0.3g/l after 20hr of deposition time and 98% of Cu was recovered on cathode. But the concentrations of Fe, Pb and Sn were constant with time. These results indicate that Cu was selectively deposited to cathode by electrowinning. The current efficiency of Cu electrowinning decreased with time.

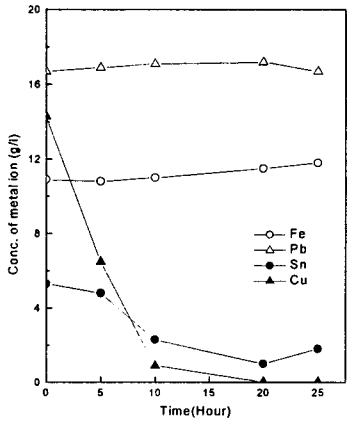

Fig. 8 Electrowinning of waste etching solution. (1.9N HNO3, 3A, electrode disatnce:1cm)

Fig. 8. Electrowinning of Cu from spent etching solution. (1.9M HNO_3, 3A)

Recovery of Sn by precipitation

After electrowinning and settling the electrolyte for 6 hours, the pH of the raffinate solution was adjusted with $Ca(OH)_2$ or $Pb(OH)_2$ as a neutralizing agent to separate Sn as a hydroxide or oxide form. Precipitate of $Sn(OH)_4$ was obtained at pH 1.3 and 80~90℃ for 30minutes. Pure SnO_2 was prepared by calcinations at 120℃ for two hours..

Recovery of Pb by Cementation

After removing nitric acid, Cu and Sn , lead(Pb) was recovered by cementation with iron powders. The effect of pH on the cementation percent of Pb with iroin powder in synthetic solution having only Pb was shown in Fig. 9 at 70°C. The cementation percent of Pb increased with pH up to pH 2.0 and about 95% of Pb was cemented. Because of NOx salt in solutions, the pH of real spent etching solutions is very low and the cementation reaction of Pb with iron powder would not occur. Therefore, the cementation experiments were carried out by adding sodium pyrosulfite($Na_2S_2O_5$) as a reducing agent. The effect of sodium pyrosulfite concentration on the cementation of Pb was shown in Fig. 10. It is seen that the cementation of Pb increased with the concentration of sodium pyrosulfite and resulted in Pb cementation percent of 95% at 6.0g/l. The reaction equation is represented as

$$4HNO_3 + Na_2S_2O_5 = 2NaHSO_4 + 4NO_2 + H_2O$$

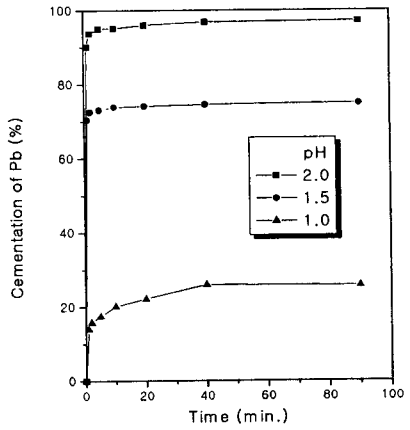

Fig. 9. Effect of pH on the cementation of Pb with Fe powders.(Pb:10g/l, 70℃, Fe:14g/l)

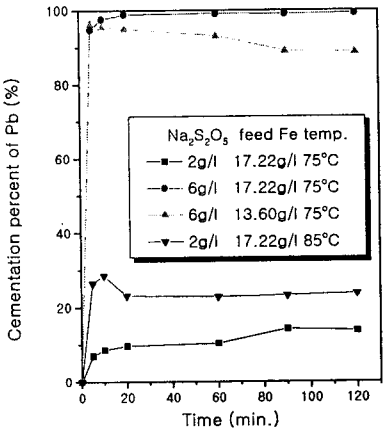

Fig. 10. Effect of the $Na_2S_2O_5$ on the cementation of Pb with Fe powder in nitrate solution. (75℃, Cu:10g/l, Pb:10g/l, pH:2.0)

Conclusions

1) Nitric acid solution was obtained in 5 stage of extraction by TBP at O/A=3.

2) Copper was obtained by electrowinning from spent etching solution after decreasing the concentration of nitric acid by solvent extraction with TBP at 3.0A and 1.9N nitric acid.

3) It was possible to separate the tin as a $Sn(OH)_4$ precipitate from the solution by adjusting the pH of the solution and pure SnO_2 was prepared by calcinations the precipitate.

4) Cementation of lead ions with iron powder from the solution removing nitric acid, Cu and Sn was performed. And a purity of 99% lead metal was obtained by adding iron powder and sodium pyrosulfite as a reducing agent.

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