Transactions of the Materials Research Society of Japan 29[5] 1769-1772 (2004)

Recovery of copper by solvent extraction from spent ammonia etching solutions- recent development in China

Dingfan Qiu, Chun Wang, Chengyan Wang
Beijing General Research Institute of Mining & Metallurgy (BGRIMM), Beijing, 100044, P. R. China
Fax: 86-10-68321362, e-mail: qiudf@cae.cn

With the development of electronic industry in China, lots of printed circuit board plants have been built in Guangdong Province, Jiangsu Province and Shanghai, China. The spent ammonia etching solutions derived from those printed circuit board (PCB) plants contain 120-150 g/l Cu and 8-9 mol/l (NH_4Cl+NH_3). Conventionally, the copper was simply recovered by chemical precipitation technique, which is thought to be less effective and environmentally unfavorable. In recent years, an environmentally benign solvent extraction technology using LIX 54 or LIX 84-I has been developed and adopted in China to recover copper and regenerate the etchant. This makes it possible to recycle the etching solution within the PCB plants and recover copper as a by-product. The situation and recent development of such technology in PCB industry of China were introduced. The technology and process were reviewed. The strategies on how to promote application and environmental concerns on using this technology have been discussed in this paper.

Keywords: Copper etching solution, Solvent extraction, China PCB Industry.

1. INTRODUCTION

In the past ten years, the electronics industry had changed dramatically in China. The average growth has been over 20% since 1995 [1-2]. Because lots of world famous electronics companies have built their manufacture plants in China, China has become one of the important electronics manufacture bases in the world. As one of the important parts of electronics industry in China, hundreds of printed circuit board (PCB) plants have been built in two regions, Zhu River and Yangzi River Deltas. The main PCB plants are located in the major cities like Shenzhen, Zhuhai, Huizhou and Dongguan in Guangdong Province; Shuzhou, Kunshan in Jiangsu Province and Shanghai.

With the development of PCB industry in China, large quantities of effluents are discharged from these plants. As environmental policies and concerns on discharge of effluents containing hazardous heavy metals or organics become more stringent in recent years in China, how to treat such effluents, thus, has become one of important issues for PCB Industry.

There are different kinds of effluents discharged in a PCB plant. One of major effluents that should be treated is spent ammonia etchant from copper etching procedure. The best solution for such etchant is to recover copper as a by-product, and regenerate and reuse the etchant.

The typical spent ammonia etching solutions derived from those plants contain 120-150 g/l Cu and 8-9 mol/l (NH_4Cl+NH_3). There are several kinds of methods adopted to treat spent etchant, such as chemical precipitation, ion exchange and solvent extraction. Chemical precipitation is to simply precipitate copper from etchant by adding acid, but it can't produce a saleable product and recycle the etchant; Ion exchange is to absorb copper from etchant by cationic resin, but the absorption capacity is relatively small. Solvent extraction can recover copper as copper salts or metals and regenerate the etchant, which can be reused in PCB plant. Of the three methods, the last one has advantages over the former ones, thus is considered to be a viable and environmentally friendly technology for recycle of spent PCB etchant, thus, should be promoted in China's PCB industry.

In this paper, the situation of PCB industry in China was introduced briefly. The technologies and processes on recycling of spent ammonia etchant were reviewed. The strategies on promotion of environmentally benign technologies were discussed in this paper.

2. PCB PLANTS, LOCATIONS AND PRODUCTIONS

In China, PCB industry's growth is about 15% per year except for in 2001. The total sales of PCB is up to US$ 4.3 billion in 2002 and estimated to be US$5.4 billion in 2003. Following United States and Japan, China ranks the third largest PCB producer in the world. In 2003, there are 662 PCB plants in China. [3-4]

Guangdong Province, southern part of China, is the major region of PCB Industry, used to account for 80-85% of total PCB production in China. 90% of PCB plants in this region were moved from Hong Kong.

In recent three years, with lots of international IT companies built their plants in Suzhou, Kunshan, Wuxi in Jiangsu Province and Shanghai, lots of upstream PCB plants have moved from Taiwan and Singapore to this region. Therefore, the growth of PCB in the eastern part of China is very rapid. This region has become the other largest PCB base in China, now accounts for 40% of total production.

The products and production of China's PCB Industry during 1995 to 2003 are shown in Table I. The total production and annual growth are shown in Figure I.[3]

Table I PCB Products and Production During 1995 to 2003 (in million m^2)

Year	1995	1996	1997	1998	1999	2000	2001	2002	2003*
SSB	11.7	12.4	13.0	13.9	15.3	16.6	16.9	18.2	19.7
DSB	3.62	4.10	4.50	5.87	6.29	6.97	6.76	7.79	8.17
MLB	1.24	2.80	4.60	6.86	12.0	16.2	16.5	21.4	28.0
FCB	-	-	-	0.25	0.86	1.23	1.89	3.26	4.89
Total	16.6	19.3	22.1	26.9	34.5	41.0	42.0	50.6	60.7

SSB: Single Sided Printed Board;
DSB: Double Sided Printed Board;
MLB: Multilayer Printed Board;
FCB: Flexible Printed Board
*Estimated

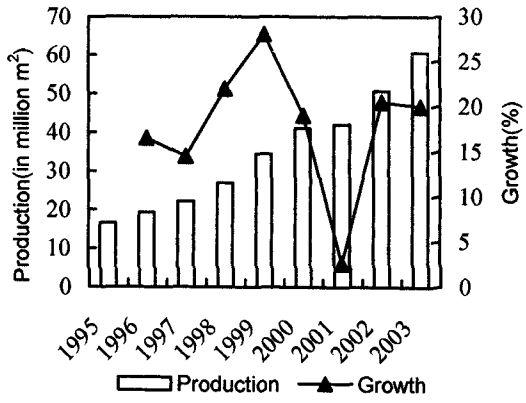

Figure I Total Production and Growth During 1995 to 2003

According to the statistics published by China Print Circuit Associate (CPCA) in 2002, 60% of PCB plants are located in Zhu River Delta, southern part of China; 30% of PCB plants are located Yangzi River Delta, in eastern part of China; the other 10% are located in northern part of China, like in Beijing, Tianjin, Dalian and Sichuan Province.

The distribution of PCB plants in China is shown in Figure II. [3]

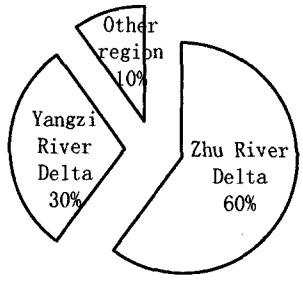

Figure II. Distribution of PCB plants in China

The top 10 PCB producers in China are shown in Table II. [3]

Table II Sales of top 10 PCB producers in China (in million US Dollar)

No.	Company	2001	2002*
1	Viasystems China	240	260
2	Elec & Eltek	240	220
3	Multek Asia	180	200
4	Shanghai Meadville (OPC)	180	178
5	Unimicron	58	145
6	Top Search	147	142
7	Compeq China	113	135
8	Eastern Pacific Circuit	138	130
9	Techwise	84	96
10	Wus China	85	88
	Total	1465	1594

*Estimated

All the top 10 PCB producers in China are solely owned enterprise of Hong Kong, United States or Taiwan. The total sales of these producers are 1.46 billions US$ in 2001, accounting for 33.7% of total PCB sales in China.

With the rapid growth of PCB industry in China, the treatment of effluents discharged from PCB plants has become a vital issue for the sustainable development of PCB Industry.

For a PCB plant with a capacity of 100,000 m^2/month, the effluents discharged is 1000 m^3 per day, 4% of these effluents, i.e., 40 m^3, is spent ammonia solution.[5] As the spent ammonia etchant contains very high content of copper and ammonia, it is one of major effluents should be treated and recycled.

The total spent ammonia etching solution discharged from these PCB plants in China is estimated to be over 200,000 m^3/a.

The treatment of spent ammonia etchant is of interest for many Chinese researchers and engineers, several processes were proposed in China. [6-20]

3. CHEMICAL PRECIPITATION PROCESSES

Chemical precipitation process is the one commonly used in PCB plants in China. The copper was simply recovered by chemical precipitation using acid.

Gao and He, Guangxi Metallurgical Institute, studied the recovery of copper from spent ammonia etchant. The proposed process flowsheet is shown in Figure III. [8]

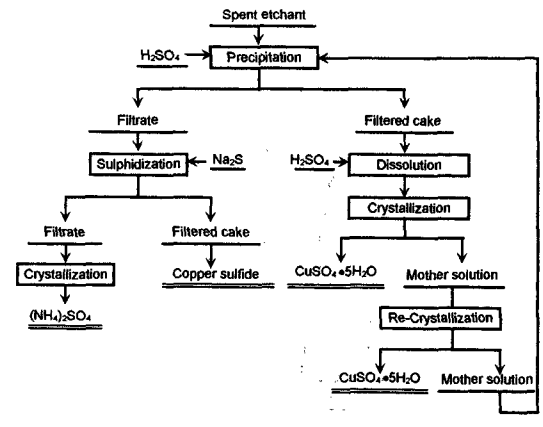

Figure III Principle flowsheet for recovering copper from spent etchant by chemical precipitation

The spent ammonia etchant is neutralized and adjusted to ~pH 5 by adding sulphuric acid, copper is precipitated as cupric carbonate. 95% of copper is precipitated, and 2-5 g/L of copper remains in the filtrate. The copper in the filtrate is precipitated as sulphide by using sodium sulphide, then is concentrated and crystallized to recover ammonia sulfate.

The resultant cupric precipitate was re-dissolved into sulphuric at pH of 2, and concentrated by heating to gravity of 1.33 g/cm^3, then cooled to room temperature to crystallize copper sulfate. The copper remaining in the mother solution was recovered further by the second crystallization. 80% of copper can be recovered in the two stages of crystallization. However, the resultant copper sulfate contains ammonia sulfate and chloride, thus should be re-crystallized to obtain a saleable product.

Zhen[10] and Zhu[12] studied the recover copper from spent etchant by adding sodium hydroxide. Copper is precipitated as hydroxide with purity of 81%. But the emission of ammonia during the addition of sodium hydroxide makes the process environmentally unfavorable. The resultant filtrate needs further treatment to meet the environmental requirement before discharge.

Jiang and Mu[13-15] proposed to recover copper from spent etchant by mixing acidic and ammonia etchant and adjusted to pH 6-6.5, the resultant precipitate is dissolved with concentrated sulphuric acid to produce copper sulfate, which needs further re-crystallization to improve purity and quality.

4. SOLVENTEXTRACTION PROCESSES

In recent years, an environmentally benign solvent extraction (SX) technology using LIX 54 (β-diketone) or LIX 84-I (2-hydroxy-5-nonylacetophenone oxime) has been developed and adopted in China to recover copper and regenerate the etchant. This makes it possible to recycle the etching solution within the PCB plants and recover copper as a by-product. Several works using SX technology for such purpose have been published. [16-19]

Huang and Ling studied the extraction of copper from a real spent etchant containing Cu 107.39 g/L, NH_3 128.4 g/L and chloride 108 g/L. [16] The copper in the etchant can be reduced below 30 g/L by 3 stages of extraction using 40% v/v LIX 54 at phase ration (O/A) of 8/1.

Gu and his co-workers studied the extraction of copper from a real spent etchant containing 157 g/L Cu, 179 g/L NH_4^+ and 169 g/L Cl^-. The maximum loading capacity of 80% of LIX 54-100 was measure to be 88.9 g/L of Cu. 82% of copper can be extracted by 3 stages of extraction with 80% v/v LIX 54-100 at phase ration (O/A) of 2/1. 80% of loaded copper can be stripped with 180 g/L H_2SO_4 in one stage at phase ration (O/A) of 2/1. Free ammonia in the PLS was found to depress copper extraction.

On the basis of the test results, a simplified process was proposed as shown in Figure IV. Copper in the spent etchant is recovered by 80% v/v LIX54-100 in one stage extraction at phase ratio of 2/1, the raffinate containing 73 g/L copper is recycled to etching operation. The loaded organic is stripped with sulphuric acid. The resultant strip liquor contains 70-80 g/L of copper, is crystallized to produce copper sulfate. The mother solution is recycled to stripping stage.

The process is simple and efficient. The organic, etchant and strip agent are recycled within the circuit. No wastewater is discharged from the circuit.

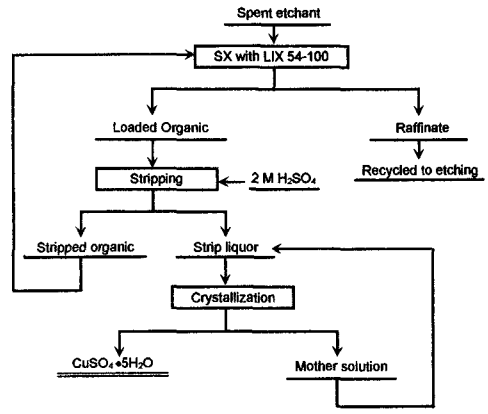

Figure IV Simplified Process for recovery of copper form spent ammonia etchant with 80% LIX 54-100 [17]

Liu Daxing and her co-workers of Beijing General Research Institute of Mining & Metallurgy (BGRIMM) proposed a process for recovering copper from spent ammonia etchant with LIX84-I. A demonstrate SX plant with a capacity of 2-3 m^3 of etchant per day was commissioned in Zhuhai, Guangdong Province. [18]

The principle flowsheet is shown in Figure V.

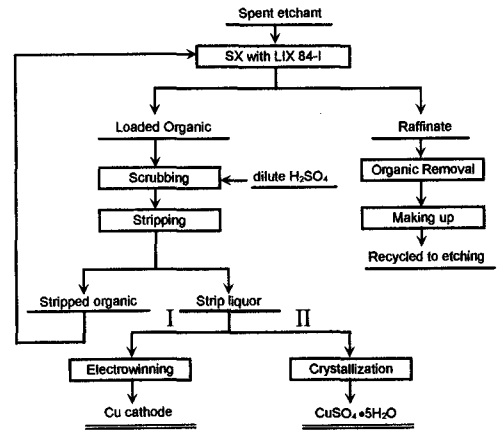

Figure V Principle flowsheet for recovering copper from spent ammonia etchant with LIX 84-I[19]

The copper in the spent etching solution can be reduced to less than 20 ppm by using three stages of extraction at high phase ratio. The raffinate is passed through a flotation cell and dual media filter to remove entrained organic, and made up with ammonia and other additives, then recycled to etching operation.

The free ammonia in feed can decrease copper extraction, especially at concentration higher than 100 g/L.

To remove physical entrained and chemical absorbed ammonia or chloride and ensure the quality of copper by-product, 3 stages of scrubbing was adopted. The

scrub liquor is made up with sulphuric acid and deionized water. 90% of ammonia and chloride can be removed from organic by controlling pH of scrub liquor.

The scrubbed organic then is stripped with sulphuric acid of 160-170 g/L Depending on marketing demand, the resultant strip liquor can be used to produce copper cathode by electrowinning or sulfate by evaporation and crystallization.

The capital cost and operating cost for a SX plant with capacity of 3 m^3 per day are estimated. The capital cost is about US$ 90,000 to 100,000. The operating cost is US$ 800 per ton of copper.

The plant has been run well for 2 years. It is demonstrated the SX technology with LIX 84-I for recovery of copper form spent ammonia etchant is simple, highly efficient, profitable and environmentally friendly. From viewpoint of resource circulation and environmental protection, the SX processes should be promoted in PCB industry in China.

5. STRATEGIES FOR PCB ETCHANT RECYCLING IN CHINA

In the past ten years, PCB industry has been grown dramatically in China. Lots of PCB Plants sell directly the spent etchant to the low-level facilitated treatment plants, where copper is simply precipitated as copper sulfate, and large quantities of wastewater containing heavy metals, ammonia and chloride are discharged.

To improve situation of etching recycling in China, the following things should be considered:

- In a PCB plant, the spent etchants should be classified before they are treated and discharged. According to the characteristics of effluents, different effluents should be treated by different processes to improve efficiency,
- PCB is a high investment, high technology and high repayment industry. To keep the sustainable growth of PCB, the treatment capacity of spent etchant should match the growth of PCB. Government should encourage and support the domestic PCB industry to improve their facilities and competitive ability by making favorable policies,
- Shut down of the small scale PCB plants whose discharged effluents can't meet the requirement of state's standard and limitations,
- Promoting the development of clean and effective technologies and equipments for etchant recycling, and improving comprehensive utilization level of spent etchant,
- Effective management of PCB etching recycling market. Government should make favorable policies on loan and tax cutting for etchant recycling enterprises,
- Building a spent etchant treatment center in big PCB zone, and making such center operate environmentally sound and profitably. This pattern will be beneficial to sustainable development of PCB industry and environmental protection.

6. CONCLUSIONS

Recovery of copper from ammonia PCB etching solution by solvent extraction is a feasible way to extract copper and regenerate etchant. In China, at least 85% PCB plants adopt simple chemical precipitation processes to treat PCB effluents. These will result to big environmental pollution. Solvent extraction technology has a potential in recovery of copper from spent ammonia etchant. It has been demonstrated to be environmentally benign in China. Government should make favorable policies to promote it application by encouraging PCB industry to invest on etchant recycling, and cooperating with them to build regional treatment center to process effectively the spent etchant in PCB industry zones of China.

REFERENCES

[1] Q. Wen and M. Liu, Jiangshu Chemical Industry, 24(6), 4-8(1998).

[2] "The 2002 Yearbook of Electronics Industry of China", Electronics Industry Publisher, Beijing (2002) pp.28-30.

[3] "Research Report on Market of PCB Industry in China", China's Electronics Associate Information Center, Beijing (2003), pp.21-80.

[4] Z. He, Shanghai Nonferrous Metals, 21(1), 34-38 (2000).

[5] A. Luo. Technology & Development of Chemical Industry, 31(3), 46-48 (2002).

[6] S. Shi. Printed Circuit Board Information, 5, 18-25 (1995).

[7] C. Mu. Water Supply & Discharge, 12, 19-21 (1995).

[8] S. He and L. Gao, Guangxi Chemical Industry, 28(2), 56-58 (1999).

[9] J. Han, Y. Wu and Z. Xue, Comprehensive Utilization of Resources, 5, 14-15 (2000).

[10] S. Zhen and Q. Tang, Chemical Industry & Environmental Protection,17 (1), 45-47 (1997).

[11] Y. Zhao, Industrial Waste Water Treatment, 17(1), 407-408 (1997).

[12] D..Zhu, F. Wen and F. Yue, Science of Environmental Protection, 25(1), 13-15 (1999).

[13] G. Mu and Y. Jiang, J. Guangxi University, 22(3), 222-224 (1997).

[14] G. Mu and Y. Jiang, J. Guangxi University, 23(1), 222-224 (1998).

[15] Y. Jiang, X. He and G. Mu, Environmental Engineering, 16(5), 62-64 (1998).

[16] S. Huang and Y. Ling. Engineering Chemistry & Metallurgy, 19(3), 272-272 (1998).

[17] B. Jia, G. Gu and P. Zhu, Techniques and Equipments for Environmental Protection Control, 3(11), 70-73 (2002).

[18] Y. Yi, G. Gu and B. Jia, Chemical Research & Application, 14(6), 755-757 (2002).

[19] D. Liu and Q. Luo, "Recovery of copper from spent PCB ammonia etchant", Proceeding of '2002 Cognis LIX User Conference of China, Cognis/BGRIMM, Kunming (2002), pp.79-82.

(Received October 10, 2003; Accepted October 31, 2003)