Printed Circuit Board Recycling Methods

1. Introduction to Printed Circuit Boards

The Printed Circuit Board (PCB[1]) manufacturing process is very complicated, involving many special chemicals and valuable materials. These materials discharge into the environment in the forms of wastewater, spent solution and solid waste. After years of research endeavors by academia, research institutes and the recycling industry, many valuable resources have been identified and the recycling of these resources have been very successful in commercial scale. Recycling of resourceful wastes generated by the printed circuit board industry includes (1) recovery of copper metal from edge trim of printed circuit boards, (2) recovery of tin metal from tin/lead solder dross in the hot air leveling process, (3) recovery of copper oxide from wastewater treatment sludge, (4) recovery of copper from basic etching solution, (5) recovery of copper hydroxide from copper sulfate solution in the plated through holes (PTH) process, (6) recovery of copper from the rack stripping process, and (7) recovery of copper from spent tin/lead stripping solution in the solder stripping process.

2. Characterization of wastes from printed circuit board manufacturing

The manufacturing process for printed circuit boards is a difficult and complex series of operations. Most of the printed circuit board industries in Taiwan use the subtractive method. In general, this process consists of a sequence of brushing, curing of etching resistor, etching, resistor stripping, black oxide, hole drilling, de-smearing, plating through hole, curing of plating resistor, circuits plating, solder plating, plating resistor stripping and copper etching, solder stripping, solder mask printing and hot air leveling.

Due to the complexity of the process, various wastes are generated during printed circuit board manufacturing. Table 1 shows the amount of waste generated from a typical multilayer printed circuit board process per square meter of board. Solid wastes include edge trim, copper clad, protection film,

[1] In this document, the acronym PCB is used for Printed Circuit Boards. This document does not refer to polychlorinated biphenyls which are also commonly referred to as PCBs..

drill dust, drill pad, cover clad, waste board, and tin/lead dross. Liquid wastes include high concentration inorganic/organic spent solutions, low concentration washing solutions, resistor and ink. Figure 1 shows the ratio of major wastes generated from the printed circuit board manufacturing process.

Many spent solutions from printed circuit board manufacturing are strong bases or strong acids. These spent solutions may also have high of heavy metal content and high chemical oxygen demand (COD) values. Consequently, these spent solutions are characterized as hazardous wastes and subjected to tight environmental regulations. Nevertheless, some of the spent solutions contain high concentrations of copper with high recycling potential. These solutions have been subjected to recycling by several recycling plants with great economic benefit for many years.

Recently, several other wastes have also been recycled on a commercial scale. These wastes include printed circuit board edge trim , tin/lead solder dross, wastewater treatment sludge containing copper, copper sulfate PTH solution, copper rack stripping solution and tin/lead spent stripping solution.

Table 1: Amount of waste from multilayer printed circuit board manufacturing process

item	Waste	Characterization in Taiwan	kg/m^2 of PCB
1	Waste board	Hazardous	0.01~0.3kg/m^2
2	Edge trim	Hazardous	0.1~1.0kg/m^2
3	Hole drilling dust	Hazardous	0.005~0.2kg/m^2
4	Copper powder	Non-hazardous	0.001~0.01kg/m^2
5	Tin/lead dross	Hazardous	0.01~0.05kg/m^2
6	Copper foil	Non-hazardous	0.01~0.05kg/m^2
7	Alumina plate	Non-hazardous	0.05~0.1kg/m^2
8	Film	Non-hazardous	0.1~0.4kg/m^2
9	Drill backing board	Non-hazardous	0.02~0.05kg/m^2
10	Paper (packaging)	Non-hazardous	0.02~0.05kg/m^2
11	Wood	Non-hazardous	0.02~0.05kg/m^2
12	Container	Non-hazardous	0.02~0.05kg/m^2
13	Paper (processing)	Non-hazardous	-
14	Ink film	Non-hazardous	0.02~0.1kg/m^2
15	Wastewater treatment slurry	Hazardous	0.02~3.0kg/m^2
16	Garbage	Non-hazardous	0.05~0.2kg/m^2
17	Acidic etching solution	Hazardous	1.5~3.5 L/m^2

item	Waste	Characterization in Taiwan	kg/m² of PCB
18	Basic etching solution	Hazardous	1.8~3.2 L/m²
19	Rack stripping solution	Hazardous	0.2~0.5 L/m²
20	Tin/lead stripping solution	Hazardous	0.2~0.6 L/m²
21	Sweller solution	Hazardous	0.05~0.1 L/m²
22	Flux solution	Hazardous	0.05~0.1 L/m²
23	Microetching solution	Hazardous	1.0~2.5 L/m²
24	PTH copper solution	Hazardous	0.2~0.5 L/m²

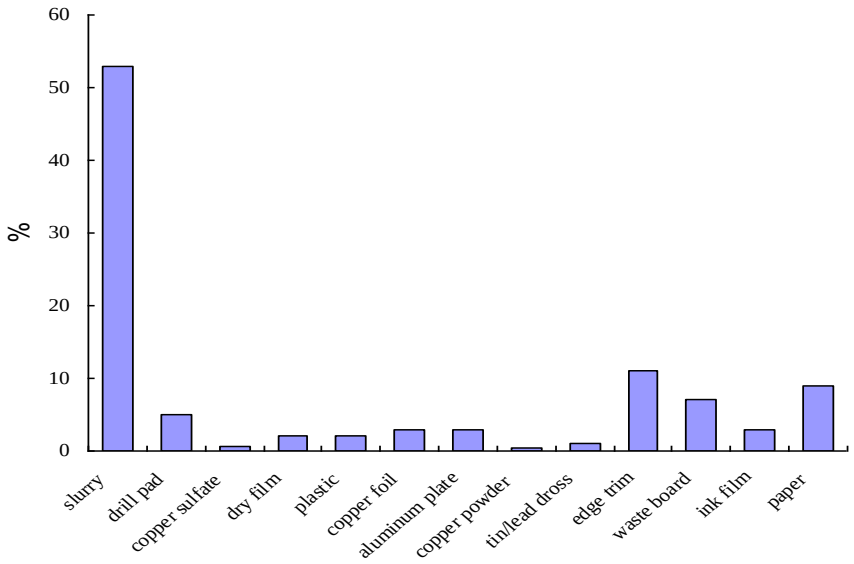

Figure 1: Proportions of wastes generated from printed circuit board manufacturing

3. Commercial resource recycling process

Due to years of study by research institutes, the recycling industry and government promotions, the recycling wastes from printed circuit board processes that contain valuable resources has been very fruitful in Taiwan. Some examples that have been reported as successful are described below.

3.1 Recovery of copper metal from edge trim of printed circuit boards

Printed circuit board edge trim has high copper content ranging from 25% to 60%, as well as precious metal content (> 3 ppm). The process for recovery of copper and precious metals from printed circuit board edge trim is similar to that from waste printed circuit boards. In general, the edge trim is

processed alone with waste printed circuit boards. The recycling process includes:

(1) Hydrometallurgy
Edge trim is first treated with stripping solution to strip and dissolve precious metals, typically gold (Au), silver (Ag) and platinum (Pt). After adding suitable reductants, the ions of precious metals are reduced to metal form. The recovered Au can be further processed to prepare commercially important potassium gold cyanide ($KAu(CN)_2$) by electrochemical methods.

(2) Mechanical separation
After the precious metals recovery, the edge trim is further processed to recover copper metal. In general, mechanical separation is involved. The edge trim is first shredded and ground. Due to difference of density, the copper metal particles can be separated from the plastic resin by a cyclone separator.

3.2 Recovery of tin metal from tin/lead solder dross

Tin/lead solder dross generated from hot air leveling and solder plating processes typically contains approximately 37% lead (Pb) and 63% tin (Sn) metals and oxides. The dross may also contain approximately 10,000 ppm of Cu and a small amount of Fe. The dross is first heated in a reverberatory furnace (1400-1600°C) and reduced to metals by carbon reduction.

$$SnO_2 + C \xrightarrow{\Delta} Sn + CO_2$$

$$2MO + C \xrightarrow{\Delta} 2M + CO_2$$

During the deslagging operation, the iron impurity is removed. In order to reach the standard of Sn63 solder, of which Cu< 0.03%, the trace amount of copper should also be removed. This can be achieved by placing the molten metal in a melting furnace with the addition of sulfur. The sulfur reacts with copper to form copper monosulfide (CuS), which can be removed as slag. The tin lead ratio is analyzed with X-ray fluorescence (XRF) and readjusted to meet standards in Taiwan by adding high grade Sn and Pb metal. Figure 2 shows the recycling process.

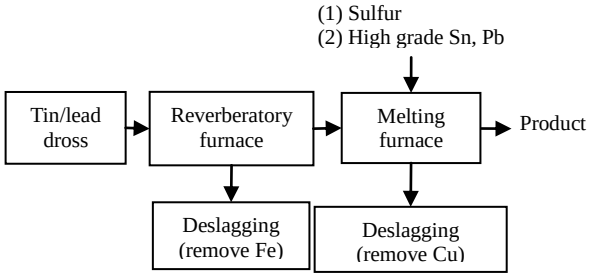

Figure 2: Tin/lead dross recycling process

3.3 Recovery of copper oxide from wastewater sludge

The wastewater sludge in the printed circuit board industry typically contains high amounts of copper (>13%, dry base). The recycling of the sludge is simple and straightforward. The general practice in the recycling industry is to heat the sludge to 600-750°C to remove the excess amount of water and to convert the copper hydroxide to copper oxide. The copper oxide is then sold to the smelter to produce copper metal. However, the current practice is energy consuming and the environmental impact should be subjected to further evaluation.

3.4 Recovery of copper from spent basic etching solution

The spent solution is generated from the etching process. Spent basic etching solution contains about 130-150 g/L of copper. The spent solution is first adjusted to a weak acidic condition, at which most of the copper ions are precipitated out as copper (II) hydroxide ($Cu(OH)_2$). $Cu(OH)_2$ is filtered and further processed to recover copper similar to that as used in sludge recycling (Section 3.3). The copper remaining in the filtrate (about 3g/L) is further recovered with selective ion exchange resins. Since the filtrate is acidic, the spent solution can be used to neutralize basic etching solution at the beginning of this process.

$Ca(OH)_2$ can also be further converted to $Cu(SO)_4$. Copper hydroxide is dissolved in concentrated sulfuric acid. After cooling, crystallization, filtration or centrifugation and drying, $Cu(SO)_4$ is obtained. Figure 3 shows the recycling process.

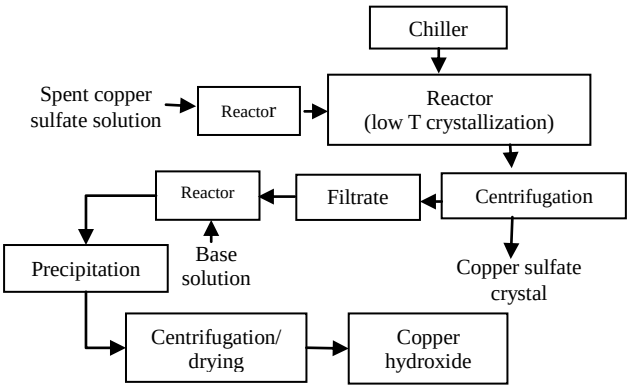

Figure 3: Recovery of copper from acidic (basic) etching solution

3.5 Recovery of copper hydroxide from copper sulfate solution in PTH process

Spent copper sulfate generated from PTH manufacturing contains copper ions at a concentration between 2-22 g/L. The spent solution is loaded into the reactor. The solution is agitated while the temperature is lowered by a chiller to 10-20°C, at which the copper sulfate crystal precipitates out of solution. The copper sulfate crystal is recovered by centrifugation. The pH of the effluent is further readjusted to basic condition to recover the remaining copper as $Cu(OH)_2$, of which the recycling process is as described previously. Figure 4 shows the process.

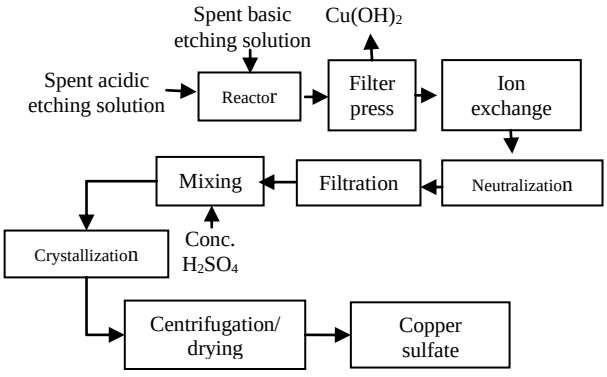

Figure 4: Recovery of copper hydroxide from copper sulfate solution in PTH process

3.6 Recovery of copper from the rack stripping process

The stripping process is done to remove copper from the rack and uses nitric acid. The copper in the spent nitric acid is in the form of copper ion.

Therefore, the copper ion (approximately 20 g/L) can be recovered directly by electrowinning. Under suitable electrochemical conditions, the copper ions can be recovered as metal copper. The other metal ions in the spent solution can also be reduced and deposited along with copper on cathode. After the electrochemical process, the nitric acid solution contains about 2 g/L of copper and some trace amount of other metal ions. The solution can be used as nitric solution to strip the rack. The stripping efficiency is not affected by the presence of the metal ions.

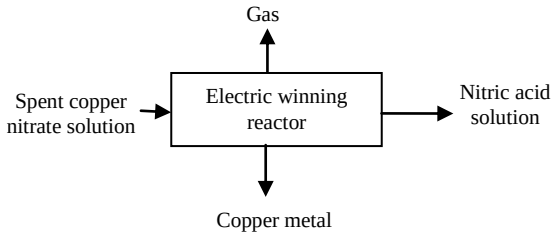

Figure 5: Recovery of copper from copper rack stripping process

3.7 Recovery of copper from spent tin/lead stripping solution in the solder stripping process

After the etching process, the protective tin/lead solder plate should be removed to expose the copper connections. Tin/lead solder can be stripped by immersing printed circuit boards in nitric acid or hydrogen fluoride (HF) stripping solution (20% H_2O_2, 12% HF). The spent solution contains 2-15 g/L Cu ion, 10-120 g/L tin ion and 0-55 g/L Pb ion. Copper and lead can be recovered by an electrochemical process. During the process, tin ion is precipitated out as oxides, which is filter pressed to recover valuable tin oxides. The filtrate is low in metal ions and can be used as tin/lead stripping solution after composition readjustment. The recycling process is shown as Figure 6.

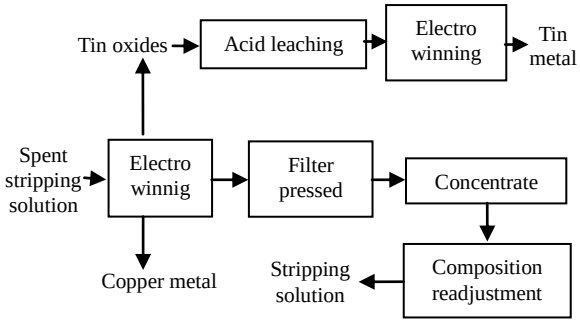

Figure 6: Recycling of tin/lead spent stripping solution

4. Current research activities

In Taiwan, the commercial recycling processes for the wastes of the printed circuit board industry mainly focus on the recovery of copper and precious metals. Although the recycling of these valuable materials is economically self-sustaining, there are many research activities focusing on the improvement of current technology in order to elevate the technology level and strengthen the compatibility of recycling industry.

4.1 Metal separation technology

Wastewater from the manufacturing of printed circuit boards contains high level of Cu2+ and small amount of other metal ions (mainly Zn2+). Separation of Cu ions from other metals can improve the purity of recycled copper. A D2EHPA-modified Amberlite XAD-4 resin prepared by solvent-nonsolvent method can remove Zn ions, leaving Cu ions in the solution. Ion-exchange isotherm showed that D2EHPA-modified Amberlite XAD-4 resin has higher Zn ion selectivity than Cu ion. The selective extraction results demonstrated that D2EHPA-modified Amberlite XAD-4 resin can separate Zn/Cu mixed ion solution. After ten batches of contacts, the relative Cu ion concentration increases from 97% to more than 99.6%, while the relative Zn ion concentration decreases from 3.0% to less than 0.4%.

4.2 Development of more innovative recycled products

As pointed out previously, Cu in wastewater is traditionally recycled as copper oxides and sold to smelters. The other alternative is to prepare CuO particles directly from wastewater. This will significantly increase the value of recycled product. CuO particles can be used to prepare high-temperature superconductors, materials with giant magnetoresistance, magnetic storage media, catalysts, pigment, gas sensors, p-type semiconductor, and cathode materials.

In order to prepare CuO nanoparticles, the wastewater is first purified to remove other ion impurities, which can be achieved by selective ion exchange resin such as D2EHPA-modified Amberlite XAD-4 resin. Figure 7 shows that the shape of CuO particle can be controlled with PEG, Triton X-100 and adjustment of solution conditions.

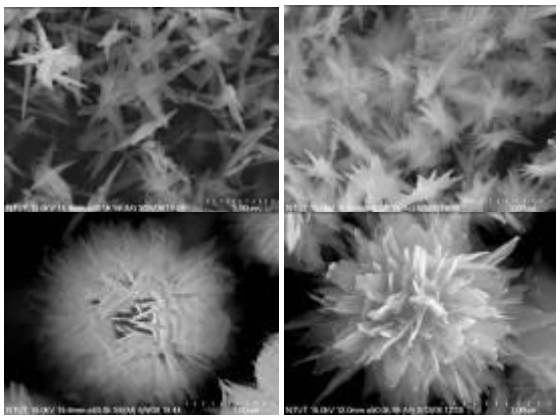

Figure 7 CuO particles with varied shape

5. Conclusions and recommendations

In Taiwan, the commercial recycling processes for the wastes of the printed circuit board industry mainly focus on the recovery of copper and precious metals. Recently, the average price of copper has risen significantly due to the imbalance of demand and supply. This is the driving force behind the successful development of the copper recycling industry in Taiwan. Nevertheless, there are still many issues that need to be addressed.

The recycling of the non-metal portion of printed circuit boards, however, is relatively small. It has been demonstrated, in a small commercial scale, that the plastic material can be used for artwork materials, artificial wood and construction materials. Nevertheless, the niche market is quite limited. Most of the non-metal wastes of printed circuit boards are therefore treated as landfill (76%-94%). In the U.S., the non-metal portions of printed circuit boards are currently used as raw materials for production by several industries. In plastic lumber, it gives strength to the "wood"; in concrete it adds strength, making the concrete lighter and providing an insulation value ten times higher than that of standard concrete. It is also being used in the composite industry as filler in

resins to make everything from furniture to award plaques. More research on this issue is needed in the future.

In view of the current commercial processes, the recycled products are not of great value. The development of more innovative recycled products will help the industry by extending the market to new terrain.

In addition to the efforts by the recycling industry, the printed circuit board industry itself should also promote and practice waste minimization. Facilities can significantly reduce waste production to minimize the secondary environmental risk of waste transportation.