Journal of Scientific Approach, **2017, 1, 6-11**
Published Online: June 21, 2017 (http://inscribepublications.com/journal/josa)
http://doi.org/10.26476/josa.2017.01.01.6-11

Recycling Technologies of PCBs

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Received April 24, 2017; Revised April 28, 2017; Accepted May 10, 2017

Abstract

Recycling of electronic circuits in general and Printed Circuit Boards, in particular, are very important for the protection of environment. It is also a good source of rare and costly metals in trace amount and proper recycling of PCBs can help recover these elements with minimum environment cost. Several recycle technologies were reviewed in this paper. From the review, it is observed that there are three main stages of PCBs recycling mainly pre-treatment, physical separation and chemical separation. In pre-treatment stage, crude separation is made and toxic parts as well as parts that can be disassembled are removed. After this process, the physical separation process starts where metallic and non metallic materials are separated after proper size reduction by appropriate technologies. Metallic and Non-metallic materials are sent for further management. Most of the time chemical separation is used to recover materials. Many scientists are also working to get metallic and non metallic parts separately and developing use of non magnetic materials as sheet so that environment can be effectively protected.

Keywords: *PCBs, recycling, corona separation, chemical separation, physical separation*

PACS Nos.: *74.62.Bf, 85.40.−e, 64.75.+g.*

1. Introduction

Modern world is producing electronics and electrical equipments at unprecedented scale as more and more services are being automated for better efficiency. Electronic gadgets have a very short life span because of the upgradation in the technology. Almost all of these gadgets contain printed circuit boards (PCBs) as their main component of circuitry. Once they are used and their life is over they are discarded. These waste known as Electronics waste (E-waste) is the fastest growing waste in the urban industrialized world. These wastes are dangerous to be dumped in landfill as they may contaminate the environment. Most of the e-waste is disposed-off by various organizations, public and private sector industries and public in general. Many developing Asian countries have also become a place to dump e-waste of developed countries.

Around 50 million tones of electrical and electronic equipment waste is generated every year. This may bring serious risks to the human health and the environment [1]. Owen *et al.*, puts this great quantity of e-waste as a crisis arising from toxic ingredients of e-waste, such as the lead, beryllium, mercury, cadmium, and brominated flame retardants (BFRs) that pose both occupational and environmental health threats [2].

PCBs provide platform for most of the electronics components and electrical connection between them like semiconductor chips, registers, capacitors and metallic inter-connections. Therefore, recycling of PCBs is important so that we recover precious metals and at the same time save environment by reusing those metals. Also proper recycling ensures that toxic ingredients of PCBs do not contaminate soil quality. PCBs typically contain lead, copper, nickel, iron, tin, palladium, zinc, silver and gold [3]. According to Duan *et al.*, waste PCBs has around 30% metal and 70% non-metals [4].

PCBs have a complex composition and therefore its recycling requires multidisciplinary approach to segregate different metals and other materials with least impact on environment. Invariably, the recycling process involves disassembly, physical recycling and chemical recycling. The present paper is to review the techniques presently being used for recycling PCBs.

2. Recycling Process

The recycling process of PCBs invariably starts with processing the waste like disassembly of toxic as well as reusable parts. Though now-a-days reusable parts in PCBs are very few as technological advancements are much faster than the shelf life of the electronic gadgets. Most of the recycling plants have manual disassembly units to get hazardous parts separately. Generally precious valuable metal components are also manually taken out.

Electronic components are also dismantled manually whenever there is a possibility of reuse. To remove electronic components most commonly impact, shearing and vibration techniques are used along with heating at the melting temperature of solders. Pyrolysis may probably occur during heating process and therefore presents a chance of dioxin formation at this stage [4].

The waste is then sent for physical separation. The process starts with size reduction, shape separation and then various processes for separating metallic and not metallic parts.

2.1. Size Reduction and Shape separation

Size reduction usually starts with cutting the PCBs into pieces of around a square centimeter area by means of shredders and granulators. Centrifugal mills and cutting mills are used for further reducing size to less than one centimeter. During the crushing process the temperatures may rises to above 250 degree Centigrade because of impacts. To effectively separate materials, the size and shape of particles is important. Al is distributed in coarse fraction (>6.5mm) and other metals are distributed in fine fractions (<5mm). Then shape separation techniques are used to separate particles as per their properties. The principles underlying this process makes use of the difference which is the particle velocity on a tilted solid wall, the time the particles take to pass through a mesh aperture, the particle's cohesive force to a solid wall, and the particle settling velocity in a liquid. Shape separation by tilted plate and sieves is the most basic method that has been used in recycling industry [5]. An inclined conveyor and inclined vibrating plate are used as a particle shape separator to recover copper from electric cable waste printed circuit board scrap [6].

2.2. Magnetic Separation

Magnetisable particle experience a force when placed under magnetic field. Magnetic separators are successfully being used to separate ferromagnetic materials, non ferrous materials and other non magnetic materials. Low intensity separators are widely used for this purpose. Iron and strong magnetic impurities are easily separated by this method. It is possible to separate copper alloys from waste by using high intensity separators.

2.3. Density Separation

Density separation techniques are useful to separate materials based on their density. Higher density materials can be easily separated from lower density materials. Material with different specific gravity move relative to their gravity. This relative movement under force of gravity and other forces introduced by air or water is used to separate the material. It is important that material are properly sized as movement in liquid is size dependent therefore to observe the best result of gravity separation materials should be properly sized [7].

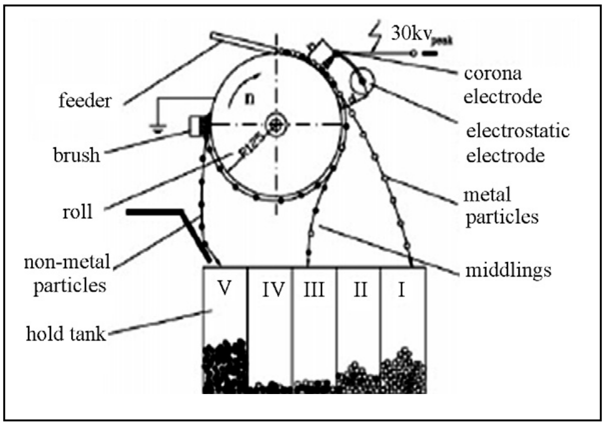

Figure 1: Corona Electrostatic Separation Technique [9]

2.4. Electric Conductivity Based Separation

This separation technique is used in separating materials having different electric conductivity. Three different techniques Eddy current separation, corona electrostatic separation and tribo-electric separation methods are used for different size of particles. Eddy current separators are used primarily for separating non-ferrous metal and non metals. The principle of operation is based on repulsive forces exerted in electrically conducive particles due to the interaction between the alternative magnetic field and Eddy currents induced by the magnetic field. These are particularly suited for coarse sized particles. Corona electrostatic separator, rotor having corona charging effect, separates raw materials into conductive and non conductive fractions. In this technique corona charge and differentiated discharge lead to different charges of particles and different forces on them. It is mainly used for recovering Copper and aluminum from chopped electric wires and cables. Tribo-electric separation is used for separating plastics depending upon their electrical properties. This separation involves charging with positive or negative charges of the components causes different force directions. It is a good technique because it is independent of particle shape [8]. Once physical separation process is over, the waste materials are further treated to obtain metal and other materials.

2.5. Chemical Recycling Process

The waste polymer material is further treated chemically to decompose it into monomer or other useful chemical composition. Pyrolysis and gasification process are used in this treatment. The pyrolysis process degrades the organic part of PCB and help in separating metallic, glass fiber and organic parts of the PCBs easily. When temperatures are appropriate, the solders melt and separation of metal part becomes easy. Proper use of this process forms gases, chars and oil that can be used as feed stock or fuel for further use or pyrolysis self sustain, but it is very complex process and may pollute environment, if not properly handled.

Recently, Zhu *et al.*, investigated an ionic liquid of 1-ethyl-3-methylimizadolium tetra-fluoroborate ([EMIM(+)] [BF(4)(-)]) as a heating medium to recover solder from waste PCBs [10]. They observed that the separation of solder from waste PCBs is complete, when waste PCBs are heated at 240°C and [EMIM(+)][BF(4)(-)] is stirred at 150 rpm for 10 min. They also observed the cross sections of waste PCBs before and after treatment with the ionic liquid, and found that there is a initial delaminating phenomenon for waste PCBs. Zhu *et al.*, concluded that [EMIM (+)] [BF(4)(-)] can dissolve bromine epoxy resins of WPCBs to some extent. This clean and non-polluting technology offers a new way of recycling valuable materials from WPCBs and prevents the environmental pollution by WPCBs effectively.

Technique of vacuum pyrolysis is also used to recover solder and metals and glass fibers from waste PCBs. Vacuum pyrolysis reduces organic vapour residence time in the reactor and lowers decomposition temperature, reducing the occurrence and intensity of secondary reactions.

Zhou and Qiu investigated a new process of "centrifugal separation + vacuum pyrolysis" for the combined recovery of solder and organic materials from waste PCBs. They found that the complete separation of solder from waste PCBs results in centrifugal separation, when waste PCBs were heated at 240°C, and the rotating drum was rotated at 1400 rpm for 6 min intermittently. Two different arrangements for recycling disassembled PCBs (10-15cm^2) were proposed. In the first centrifugal separation of solder (240°C) was followed by vacuum pyrolysis of the residue (600°C) [11] and in the second vacuum pyrolysis (600 °C) was followed by centrifugal separation of the residue at 400°C in order to collect solder ready for reuse [12]. This clean and non-polluting technology offers a new way to recycle valuable materials from waste PCBs and prevent the environmental pollution of waste PCBs effectively.

Recently Riedewald and Gallagher investigated a novel process for PCB recycling with molten salt [13]. This process uses inert stable molten salts LiCl- KCl as the direct heat transfer fluid and at the same time uses this molten salt to separate the metal products in either liquid (solder material, zinc, tin, lead etc.) or solid (copper, gold, steel, palladium etc.) form at the operating temperature range of 450-470 °C. This recovery reactor is a U-shaped pyrolysis vessel, where molten salt is used as continuous fluid. Residual salts from recovered materials were washed away using hot water. This novel reactor can take large PCBs during experiment the components of PCBs were also not removed.

2.6. Gasification and co-combustion

Gasification process converts organic materials into carbon monoxide and hydrogen by reacting with the raw material. This process occurs at high temperatures in a controlled environment with oxygen and/or steam. The gases produced during the process is itself a fuel or it can also be used or combusted in gas turbines for electric power generation. Combustion process competes with gasification. A certain amount of bromine present in the waste turns into ashes or chars while a major part is converted into combustion gases or into carbon monoxide and hydrogen where bromine can be recovered using suitable processes. Though both processes are good but Gasification is better from environmental point of view.

2.7. Recovering Metal

PCBs scrap has metal value more than 70% of their value because of high content of metals. Pyrometallurgy, hydrometallurgy and biotechnology are used for recovering metals. Cui and Zhang have reviewed different possible approaches for metal recovery from the waste [14].

2.8. Pyro-metallurgy

Pyro-metallurgy is used to recover the precious metals from PCB and is generally used to upgrade the mechanical separation process that does not efficiently recover precious metals. In this process the crushed PCBs scraps are burned in a furnace or in a molten bath to remove plastics. The refractory oxides form a slag phase together with some metal oxides. The recovered materials are further purified with chemical processing techniques. To reduce energy cost the plastics and other flammable materials of the waste are used in combustion. It was also observed that addition of NaOH as slag formation material promotes the effective separation of metals from the slag. The remaining slag in the blowing step was found to favour the separation of copper from other metals and allow noble metals to enter the metal phase to the greatest extent. The resulting slag was also very effective in cleaning the pyrolysis gas [12]. However, this process has limitations that recovery of metals of aluminum and iron transferred into slag is difficult. Also there may be risk of formation of dioxins because of presence of brominated flame retardants in the smelter feed. Special care will have to be taken to avoid this formation. Besides, pyro-metallurgy results in limited upgrade of metal value because we still need hydrometallurgical and/or chemical processing to refine the metals

2.9. Hydrometallurgy

This method is also used to recover metal from ores. First leaching is performed where soluble constituents are extracted by means of a solvent. For PCBs leaching involve acid and/or halide treatment. Acid treatment removes base metals so that the surface is free of precious metals. The solution is then subjected to concentration and purification procedures such as precipitation of impurities, solvent extraction, adsorption and ion-exchange to isolate and concentrate the metals of interest. Subsequently, metals are recovered using suitable methods like electro refining process, chemical reduction or crystallization for metal recover. It is observed that an oxidative sulfuric acid leach dissolves copper and part of silver, an oxidative chloride leach dissolves palladium and copper, and cyanidation recovers the gold, silver, palladium and a small amount of the copper [15]. Silver from sulfate medium is recovered by precipitation with NaCl. Palladium was extracted from chloride solution by cementation on aluminum, and gold, silver and palladium were recovered from cyanide solution by adsorption on activated carbon. Mechanical concentration processing is used to recover Cu, Pb and Sn. Liu *et al.*, suggested a general approach for recycling of scrapped PCB by hydrometallurgy. In this approach the crushed PCB were leached in the NH_3/Nh_5CO_3 solution to dissolve copper [16]. After the solution was distilled, the copper carbonate residue was converted to copper oxide by heating. The remaining solid residue was leached with hydrochloric acid to remove Sn and Pb. The last residue was used as a filler in PVC plastics which were found to have the same tensile strength as unfilled plastics, but had higher elastic modulus, higher abrasion resistance and were cheaper.

2.10. Bio-metallurgy

Bio-metallurgy involves the use of microbes (bacteria and archaea) in an aqueous environment to produce metals used in micro-filtration, industrial bioleaching, petrochemical recovery, waste treatment including nuclear waste and other process. Bio-metallurgy is also used to separate rare minerals from ore when using extreme heat or toxic chemical prove impractical or dangerous. Since the process of bio-mining is automatic once the appropriate microbes have been engineered, it is far less expensive than nano-mining or other methods of separating minerals on the molecular level.

Microbes have the ability to bind metal ions present in the external environment at the cell surface or to transport them into the cell for various intracellular functions. Bioleaching is applied for recovering of copper and other precious metals from ores for a long time. Research on bioleaching of metals from PCB is in its infancy but it has been demonstrated that using C. violaceum2 gold can be microbially solubilized from PCB [17]. Similarly natural acid mine drainage enriched bacterial consortium is used to solubilise copper from waste PCBs in 5 days [18]. Biosorption process is passive physio-chemical interaction between the charged surface groups of micro-organisms and ions solution. Biosorbents are prepared from the naturally abundant and/or waste biomass of algae, fungi or bacteria.

2.11. Reusing non-metallic waste of PCBs

Many researchers are trying to use non metallic waste of PCBs either by changing the polymers by chemical methods or by combusting the waste as fuel or are converted into a form that is not dangerous and then put into landfills. In a study Li *et al.*, proposed that after recovering metal parts through mechanical separations and other techniques, the rest of the non metallic parts of waste PCBs can be made into non metallic plates [19]. These plates can be used for various purposes as tiles, partitions or insulation board or as a filler in some another product. More research is required to use this waste in an environment friendly manner. The waste is a light weight in comparison to bricks and therefore the present author feels that investigation need to be done to find out whether it is feasible to use this non metallic waste of PCBs as a part of bricks along with ash that is mandatory. If proper binding agents are developed then there is a good chance that we can get light weight bricks for building partitions

3. Conclusion

Recycling of PCB is important. Different authors have experimented and suggested different approach to recycle the PCB waste. Non ferrous metals like Cu, Al, Sn etc., are abundant in PCBs and recovering them is important as a resource. Purity of metals in PCBs is almost ten times higher than that of rich content minerals. Most of recycling techniques involve mechanical and chemical methods but chemical methods have harmful effect for environment and therefore new methods need to be incorporated. Mechanical methods are mainly used for separation of various materials from PCBs. These methods include size separation, shape separation, density based separation, electrostatic separation etc. These methods are very much established and real challenge is in recycling the non-metal waste of PCBs. In a few of techniques it is combusted during pyrolysis and other mechanism but that requires state-of-the-art-technology to avoid formation of dioxins and furans. The author feels that using this non metallic part in some sort of useful by-product can solve the problem. One approach is to use this in tiles or partitions bricks as suggested by some scientists. If suitable binding agents could be found then this non metallic waste can be mixed with ash to make the hollow bricks that can be used as efficient building material as it will have lesser weight and will give insulating effect to walls. The same non metal materials can also be filled inside the hollow bricks to get better insulations. Author feels more investigations are required for using this non metallic waste for such building materials.

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