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Recycling of Electronic Wastes by Disintegrator Mills and Study of the Separation Technique of Different Materials

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The aim of this work was to study and develop the prospective method and technique for mechanical recycling of printed circuit boards (PCBs). This study describes mechanical reprocessing of PCBs in high-energy disintegrator mills in the direct and selective milling systems. The ferrous metal particles and plastic particles with non-ferrous metal particles were roughly separated by a magnetic separation technique. Several tests were made for air classification of plastic and non-ferrous metal particles. The particle size and distribution were examined by the sieve analysis and laser granulometry analysis (max 300 μm).The chemical composition of the PCB powders was studied by means of the energy dispersive X-ray microanalysis (EDS) with the Link Analytical AN10000 system. The X-ray mapping technique was used to evaluate element distribution inside the powder particles.
Keywords: recycling, electronic wastes, disintegrator milling, plastic powder.

1. INTRODUCTION

Recycling of post-consumer products is becoming increasingly important as an industry response to public demands that resources should be conserved and the environment should be protected. The targets of a minimum reuse, recycling, and recovery on WEEE are settled in the Directive 2002/96/EC that includes all the components, sub-assemblies and consumables that are parts of a product at the time of discarding. RoHS Directive (2002/95/EC) does affect the manufacturers, sellers, distributors, and recyclers of electrical and electronic equipment, which contain lead, mercury, cadmium, hexavalent chromium, or polybrominated diphenyl ethers. Depending upon the use and design of the particular PCB, various other metals may be used in the manufacturing process, including lead, silver, gold, platinum, and mercury. One of the ways of recycling electronic wastes is to produce powdered materials from end-of-life products. Dismantling processes and recycling of PCBs from electronic scrap were discussed in a recent study [1]. Printed circuit boards (PCBs) are common components of many electronic systems built for both military and commercial applications. PCBs are typically manufactured by laminating a dry film on a clean copper foil, which is supported on a fibreglass plate matrix. The film is exposed to the film negative of the circuit board design and an etcher is used to remove the unmasked copper foil from the plate. Solder is then applied over the unetched copper on the board [2].

PCBs are potentially a difficult waste material to process since they generally have no use once they are removed from the electrical component in which they were installed. In addition, they typically consist of the materials classified as a hazardous or "special" waste stream. They must be segregated and handled separately from other non-hazardous solid waste streams. As an alternative to off-site disposal, PCBs can be handled and processed to recover the value of the raw materials that are used to produce the boards.

For recycling PCBs there are several chemical and mechanical methods available. Chemical methods mainly include:

– pyrolysis and combustion;
– hydration and electrolysis.

The mechanical methods of PCB recycling include:

– size reduction by shredders, hammer mills;
– screening: rotating screen, or trammel, vibratory screening;
– shape, density and magnetic separation;
– electric conductivity based separation, such as Eddy Current separation, corona electrostatic separation, and triboelectric separation;

This work is mainly focused in mechanical recycling methods. The size reduction equipment for mechanical recycling PCBs from the end-of-life durable goods will include the following advantages: it accommodates large amounts of metal, handles tough engineering plastics in reasonable throughputs, liberates moulded-in and well-adhered materials, it does not embed or encapsulate foreign materials, it produces uniform particle shapes and sizes, requires low maintenance costs, it is easy to clean because of the switch-overs of material, it produces low noise and has reasonable power requirements [3].

In addition to traditional mechanical direct contact milling methods (ball-milling, attritor milling, hammer milling, etc.), PCBs can be reprocessed by the collision method.

The fracture of particles in collision with the milling component of one of the rotating rotors is called disintegration. The theoretical studies on milling by the collision method, which were conducted at Tallinn University of Technology (TUT), were followed by the development of the appropriate devices, called disintegrators, and the dif-

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ferent types of disintegrator milling, the DS-series systems [4]. Depending on the design of the disintegrator systems, the direct, separative and selective types of milling are available to be used in powder production. Direct milling suits best for testing the properties of materials or producing materials with a wide granulometry, it is used for the treatment of dry, damp and liquid materials. Separative milling is meant only for dry materials, it yields materials with a high degree of fineness and a narrow granulometry [5]. Selective milling is suitable for the treatment of multi-component materials, such as the components of industrial and domestic wastes, etc. The main kinematic parameter in the processing of materials is the specific energy of treatment E_s in kWh per ton, both in view of the size reduction effect and the economic aspect of the process [6]. The size reduction of PCBs as a function of the particle size of the specific energy of treatment was studied.

2. EXPERIMENTAL

2.1. Materials to be reprocessed

Printed circuit boards are mainly produced from thermosetting resin (epoxy or phenolic resin) and reinforced with fibres such as paper, wood, textile, and glass (of high performance).

PCB consists of ~72 wt. % of organic substance and ~28 wt. % of metals (see Fig. 1).

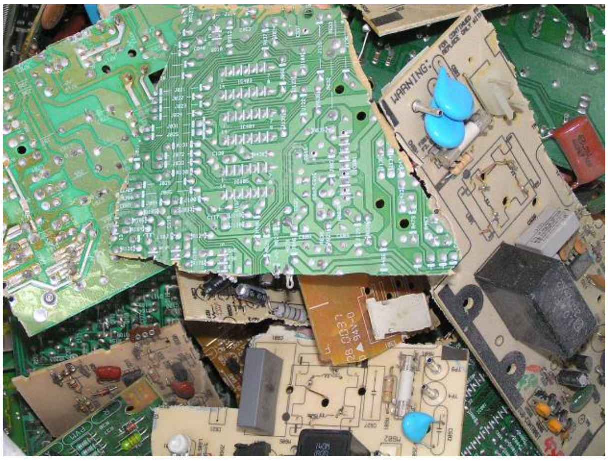


Fig. 1. Preliminarily crushed PCBs separated from dismantled post-consumer electronic equipment

The main composition of the organic substance is the ethoxyline resin bromide or ethoxyline resin chloridate. Many PCBs are made up of either polymer films such as polyimides, or less frequently polyethylene terephthalate or polyethylene naphthalate, or glass fibre composites bonded with a thermoset resin. Common resins include difunctional epoxy resins such as bisphenol, multifunctional epoxy resins such as phenol and creosol based epoxy novolacs, BT epoxy blends, cyanate esters, and polyimides. The most common hardener is dicyandiamide, diamino-diphenyl sulfone and diamino-diphenyl methane are also used [7].

Depending upon the use and design of the particular PCB, various other metals may be used in the manufacturing process, including lead, silver, gold, platinum, and mercury. The scrap of PCBs contains multi-elements: Al (2.8 mass %), Cu (10.0 mass %), Pb (1.2 mass %), Zn (1.6 mass %), Ni (0.85 mass %), Ag (280 ppm), Au (110 ppm) [8].

The purity of precious metals in PCBs is more than 10 times higher than that of rich-content minerals. Therefore, recycling of PCBs is an important subject not only from the treatment of waste but also from the recovery of valuable materials [9].

2.2. Reprocessing technology

Milling by collision means that the mechanisms of the particle size reduction of the ductile and brittle materials are different. The milling of brittle materials by collision results in a direct fracture. When milling ductile metallic materials at the initial stage, the metal will be hardened and the fatigue fracture will occur [6]. The separation systems in the DS-series disintegrators are based on the aerodynamic forces. A special inertial classifier with a closed air or gas system has been developed [10]. This system is autonomous and ecologically clean due to the use of kinetic energy in the output material. The system does not need any additional devices of transportation or fans. For various materials and disintegrator milling systems, different inertial classifiers have been designed and developed as an axial inertial classifier and a classifier with a grid formed by the row of blades (see Fig. 2.) [11, 12].

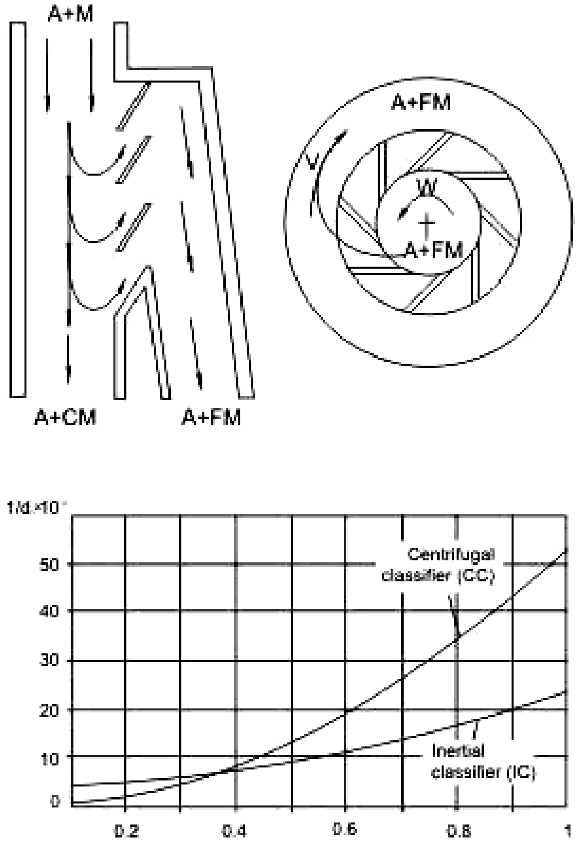


Fig. 2. The principal schemes of the inertial (air) classifier and centrifugal classifier

The reprocessing technology of the PCBs in disintegrators consisted of the following stages:

– the preliminary size reduction of the PCB plates by the experimental DSL-158 disintegrator (up to 2 times);

- the intermediate milling for the size reduction in the semi-industrial disintegrator DSA-2 (up to 6 times);
- the final milling by the DSL-115 disintegrator system in the selective milling conditions to separate the plastic and metallic components.

2.3. Characterization of the milled product

The particle size and distribution in the milled powders were examined with the help of two methods:

- sieve analysis (particle size more than 100 μm);
- laser granulometry analysis by Laser particle sizer Analysette 22 Compact (max particle size 300 μm)

To characterize the material, a scanning electron microscope (SEM) JEOLJSM-840A was used. The chemical composition of the PCB powders was studied by means of the energy dispersive X-ray microanalysis (EDS) with the Link Analytical AN10000 system. The X-ray mapping technique was used to evaluate element distribution inside the powder particles.

3. RESULTS AND DISCUSSION

3.1. Properties of the milled product

The results of the preliminary size reduction, intermediate and final milling are given in Fig 3. The medium particle size of the plastic component from a PCB after a 2-stage milling is about 5 mm – 10 mm, after 1 – 2 times of milling in the disintegrator DSA-2 it is around 1 mm. The subsequent continuous milling (6 times) in DSA-2 reduced the medium particle size to 0.45 mm. As the medium particle size and mass distribution were similar after the 6th and the 8th milling in DSA-2, the new equipment DSL-115 for further size reduction was used. The next remarkable size reduction occurred after the 4th milling in DSL-115, the medium particle size being 0.12 mm.

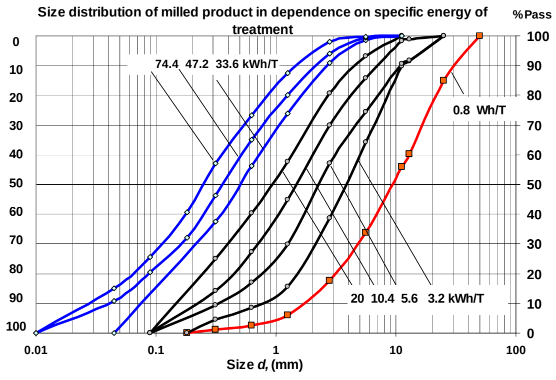


Fig. 3. Dependence of the particle medium size of PCBs on the specific energy of treatment

The powder particles from the PCB after the preliminary size reduction were mainly lamellar after preliminary milling and they stayed lamellar after the multi-stage milling (up to 8 times) in the disintegrator DSL-115. The mechanism of the fracture of PCB particles was the same after preliminary and final milling.

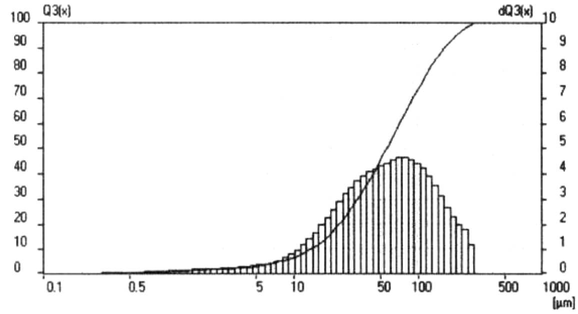


Fig. 4. Laser granulometry of the milled PCB powder

The particle size and distribution of the fine material (70 wt. %) obtained from the 8th milling in DSL-115 (0 mm – 0.3 mm) was determined by Laser Granulometry (see Fig. 4). The arithmetic mean diameter of the particle is 74 μm.

3.2. Separation of materials

After two times precruching in DSL-158 disintegrator the 8 wt. % of ferrous metals were separated from milled product by magnet. During the intermediate milling in DSA-2 disintegrator mill the amount of separated ferrous metals was decreasing from 6 wt. % (after 1st milling stage) to 2 wt. % (after 8th milling stage). During the final milling in DSL-115 disintegrator the amount of separated ferrous metals was less than 1 wt. %. It was obvious that the effectiveness of magnetic separation is depending on the size of milled product. AS the particles size of the PMMA powder varied on a large scale, the powder was classified by sieving into 7 fractions: (– 0.125 mm; + 0.125 – 0.315 mm; +0.315 – 0.63 mm; +0.63 – 1.25 mm; +1.25 – 2.5 mm; +2.5 – 5.6 mm and 5.6 – 11.2 mm) by sieving. The ferrous metals were separated in every fraction by a magnet (except fraction 0 – 0.125 mm).

The magnetic separation of the ferrous metals gave sufficiently good results (1.2 – 5 wt. %) for fractions with a larger particle size (see Figs. 5 – 7), but for fractions less than 0.63 mm the separation was less effective because of the particles were adhering to each other.

Fig. 5. Separated non-ferrous metals and composite plastic from the coarse fraction +1.25 – 2.5 mm

Fig. 6. Separated ferrous metals from the coarse fraction +1.25 – 2.5 mm

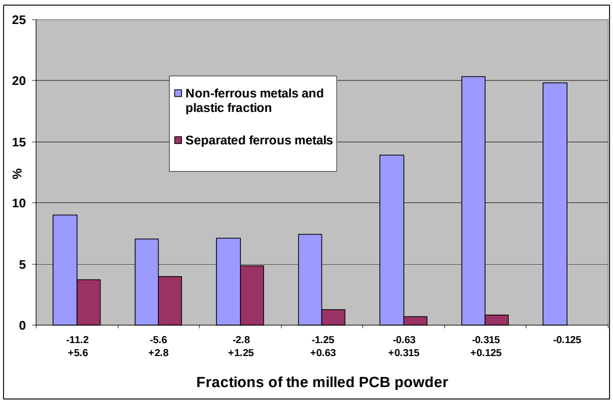
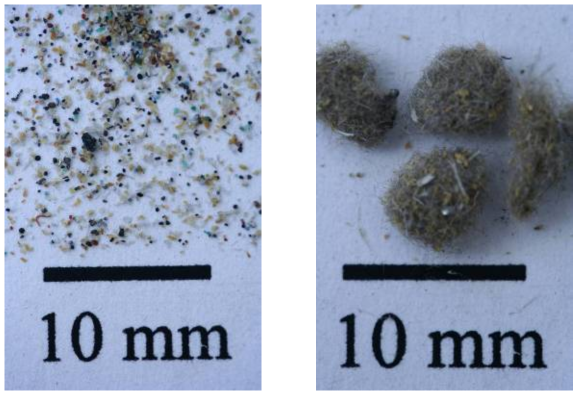


Fig. 7. Results of magnetic separation

The final milling was done by the DSL-115 disintegrator system in the selective milling conditions to separate the plastic and metallic components by air classifier.

The separation of plastic and metallic components of the milled PCB powder was not successful, only a small amount of tinfoil and fibres were separated (see Fig. 8).



a b

Fig. 8. PCB milled product after 8-time milling in DSL-115: a – separated PCB-powder particles, b – separated glass-fibre

The reason of the poor results could be a small difference in the specific weight of the powder particles. To study the chemical composition of the PCB milled powder the EDS analysis was performed.

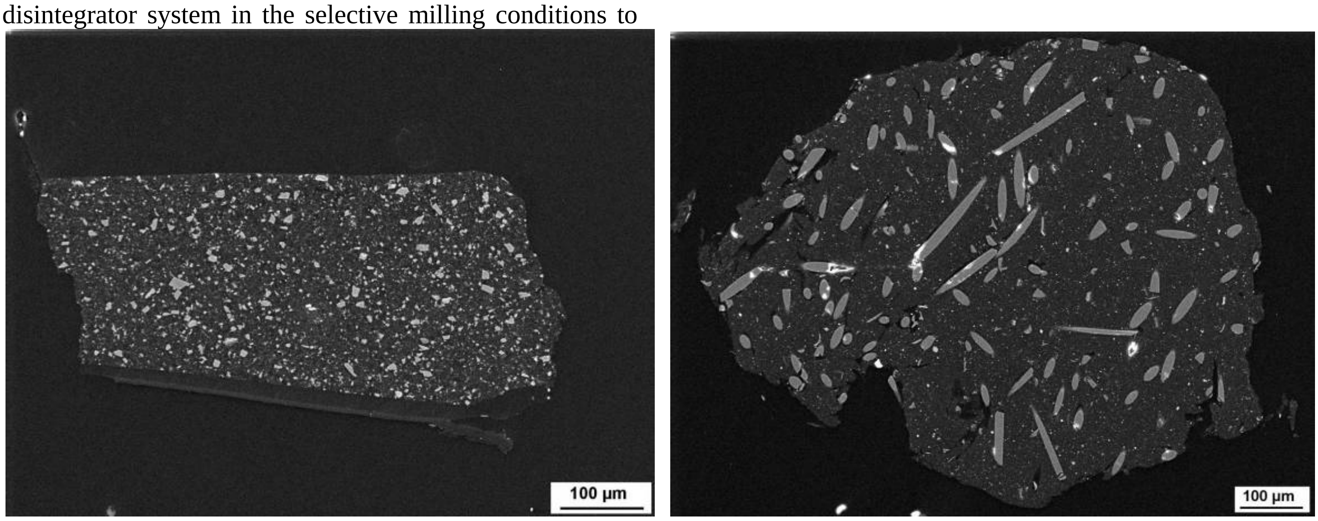


Fig. 9. EDS photos of PCB powder particles: a – green plastic matrix with 5 µm – 10 µm $CaCO_3$ crystals inside, b – black plastic matrix with Al – 7; Si – 24;Ca – 15 fibre

3.3. EDS analysis of the milled PCB powder

The sample of the PCB milled powder was prepared with the help of SEM. In the sample the plastic and metallic fractions were separated and weighed. The powder contained 29 % metallic content. The micro polish of the sample was made for the EDS analysis. Oxygen was calculated by the difference of 100 %. The chemical composition of the milled PCB powder particles was analyzed by EDS, with the results given in weight percentages.

As it follows from Table 1, most of the plastic particles are containing different metallic crystals or grains (see Fig. 9).

4. CONCLUSIONS

1. The best results of PCB waste reprocessing by disintegrators will enable a remarkable size reduction after two stages of preliminary crushing and four stages of intermediate milling.

Table 1. Chemical composition of PCB powder particles by EDS analysis

Object No.	Composition, wt %	Description
11	Ca – 38; Mg – 0.4; O – 61.4	Green plastic matrix, 5 µm – 10 $CaCO_3$ crystals inside
19	Al – 33; O – 67	Blue plastic matrix, 10 µm – 100 µm Al particles inside
23	Si – 45; O – 55	Black plastic matrix, 10 µm – 100 µm SiO_2 grains inside
25	Al – 7; Si – 24; Ca – 15; Ti – 0.4; O – 53.6	Black plastic matrix with Al – 7; Si – 24;Ca – 15 fibres
32	Cu – 65; Zn – 35	CuZn35 brass, on the edge Sn – 90; Pb – 10
41	Sn – 84; Pb – 15,8; Al – 0,2	Sn80 – Pb20 solder
61	Cu – 98	20 µm thick Cu stripe with white plastic particle
84	Pure Al	5 µm – 10 µm thick Al stripe

2. Larger metal particles and thin foil stripes from condensators can be separated by sieving. The ferrous metallic components of coarse fractions can be separated with magnets. For fine fractions (– 0.63 mm) the magnetic separation is poor.
3. The study of the chemical composition of the PCB powder particles showed that in the plastic particles metallic grains or crystals are in the matrix and because of that they cannot be separated by density separation or the air-classificator system.
4. The separation of the plastic and metallic parts of the milled multi-material in the selective milling conditions needs an additional study to determine the optimum milling parameters and in the design of new wet classifiers accounting for the densities of plastic and metallic particles.
5. The separated ferrous metals can be recovered by metallurgical methods. For separation and recovery of non-ferrous metals from milled material the pyrometallurgical or hydrometallurgical methods could be applied.

REFERENCES

1. **Hall, W. P.** Separation and Recovery of Materials from Scrap Printed Circuit Boards, Resources Conservation and Recycling (2006), doi:10.1016/j.resconrec.2006.11.010.
2. Printed Circuit Board Materials Handbook. McGraw-Hill Professional, 1997, 784 p.
3. **Biddle, M. B., Dinger, P., Fisher, M. M.** An Overview of Recycling Plastics from Durable Goods: Challenges and Opportunities *Identiplast II Conference Proceedings,* APME, Brussels, April 1999.
4. **Tamm, B., Tymanok, A.** Impact Grinding and Disintegrators *Proceedings of Estonian Academy of Scences, Engineering* 2 1996: pp. 209 – 223.
5. **Tymanok, A., Kulu, P.** Treatment of Different Materials by Disintegrator Systems *Proceedings of Estonian Academy of Scences, Engineering* 5 1999: pp. 222 – 242.
6. **Tymanok, A., Kulu, P., Goljandin, D., Roshchin, S.** Disintegrator as a Machining Device of Metal Chips to Metal Powder *In Proceedings of III ASM International Conference of the Recycling of Metals. Barcelona,* 1997: pp. 513 – 522.
7. **Bernardes, I. B. A., Rodriguez, D.** Recycling of Printed Circuit Boards by Melting with Oxidising/Reducing Top Blowing Process *In Proceedings Sessions and Symposia Sponsored by the Extraction and Processing Division,* TMS Annual Meeting, B. Mishra, Ed., Orlando, FL, February 9 – 13, 1997: pp. 363 – 375.
8. **Zhang, S., Forssberg, E.** Electronic Scrap Characterization for Materials Recycling *Journal of Waste Management and Resource Recovery* 3 1997: pp. 157 – 167.
9. **Cui, J., Zhang, L.** Metallurgical Recovery of Metals from Electronic Waste: A Review *Journal of Hazardous Materials*: doi:10.1016/j.jhazmat. 2008.02.001, 2008.
10. **Tymanok, A., Tamm, J., Roes, A.** Flow of Air and Particles Mixture in a Disintegrator *Proceedings of Estonian Academy of Sciences, Physics Mathematics* 43 (4) 1994: pp. 280 – 292.
11. **Tymanok, A., Kulu, P., Goljandin, D., Roshchin, S.** Disintegrator as a Machining Device of Metal Chips to Metal Powder *In Proceedings of III ASM International Conference of the Recycling of Metals,* Barcelona, 1997: pp. 513 – 522.
12. **Tymanok, A., Kulu, P., Goljandin, D.** Metallic Powders Produced by Mechanical Methods *Materials Science* (*Medžiagotyra*) 9 (2) 1999: pp. 3 – 7.

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