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# Analytical Study on the RoHS of Plastic from Waste Electrical and Electronic Appliances

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**ABSTRACT:** This study was conducted to identify emission characteristics of certain hazardous substances contained in the plastic of used home electrical and electronic appliances keeping in view compliance with the Restriction of Hazardous Substances (RoHS) Directive and to estimate the possibility of safe recycling practices. According to the results, the concentration of cadmium, lead, mercury and chromium were found below than Maximum Concentration Value (MCV) of RoHS, while the concentration of total bromine (T-Br) was exceeded the standard limitations in the samples of plastic from e-waste. Over 90% of the plastics used in housing cover of display electronic products were composed of Polystyrene (PS) 53.9% and PS-flame retardants 36.4%.Peak of each hazardous substance in total samples also showed higher values of bromine, cadmium and lead. In order to enhance cleaner recycling of waste electronic appliances in accordance with the allowance of RoHS Directive, the use of brominated flame retardants in plastic and chrominated synthetic resins should be restricted and applications of metal surface finishing such as coating and painting of high molecules synthetic resins should be minimized.

**Key words:** Hazardous substances, Flame retardants, Cleaner recycling

## INTRODUCTION

The Restriction of Hazardous Substances (RoHS) is a Directive to regulate the use of certain environment hostile substances in the manufacture of electrical and electronic equipment (EEE). These substances are lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs). Based on RoHS guidelines, the maximum permissible concentration of these chemicals in waste electrical and electronic equipment (WEEE) has been limited. The RoHS Directive came into force in July 2006, with the primary objective to improve implementation and enforcement of laws relating to electrical and electronic equipment with ultimate aim at solving problems of e-toxic waste (Zangl *et al.,* 2011; Townsend, 2011; Kahat and Kim, 2008). A study based on Life Cycle Assessment (LCA) of goods manufactured of plastic clearly showed that recycling of plastics originating from WEEE products demonstrated obvious advantage compared to the incineration of plastic waste (Roland and Isabelle, 2010). However, plastic recycling, particularly the plastic originated from WEEE, is not uncontested because of the potential dissipation of hazardous substances contained in recycled plastics (Sepulveda *et al*., 2010). Also, presence of these substances can give rise to high processing costs, depending on the disposal or recovery route (Wager *et al.,* 2010). Another study (Schlummer *et al.,* 2007) discussed a technological approach consists of a density based enrichment of styrenics, which are subjected to a solvolysis process (CreaSolv process) to produce recycled products that complied with the threshold values defined by the European Directive on RoHS.

According to a scientific report, the share of plastic in WEEE overall categories is estimated to around 20.6% (Huisman *et al.,* 2008). In South Korea, products of electrical and electronic industries are taken as one of the biggest markets in the country (Yoon and Jang, 2006) and after use of such products should considerably be revitalized. In spite of proper use of hazardous materials in the country, the database and information on raw materials, components and particularly waste materials of

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electronic equipment by Extended Producer Responsibility (EPR) system are still insufficient (Chung and Suzuki, 2008; Philips, 2009; Yu and Hills, 2008). In such scenario, there are ample chances that a recycled product can be reprocessed as raw material by complementing deficient information causing harm to the recycling industry in the country.

Therefore, this study is commissioned to suggest the direction of recycling and assist to make a positive decision in using components derived from WEEE through analysis of major hazardous materials. The different plastic used in WEEE and their contents of hazardous substances regulated by the RoHS Directive were identified by means of laboratory scale research. In particular, the study intends to suggest considerations following which plastic recycling can be made environment friendly with regard to the use of hazardous substances in South Korea.

## MATERIALS & METHODS

Sampling and analysis process were classified based on year of production, manufacturer, parts and quality of materials of waste display products, separated and collected by EPR system and garbage disposal system of recycling companies dealing in electronic waste. In order to indentify whether it satisfies Directive on the RoHS or not, the six hazardous substances contained in WEEE were analyzed by Energy Dispersive X-ray (EDX) fluorescence Spectrometer method and the recyclability was estimated by clarifying each parts and quality of material.

Among the guidelines on the use of certain hazardous substances, RoHS Directive has become the most representative dealing in environmental regulations. The main points discussed in RoHS Directive are Homogenous Material (HM) and Maximum Concentration Value (MCV). It involves that HM as a sample in the test for analyzing hazardous substance should have identical composition, and it should be minimum substance which cannot be separated by mechanical separation including unscrewing, cutting, grinding, abrasive process and others (Wager *et al.,* 2009). HM plays a role as an accounting standard for MCV. In case of MCV, it is allowed to include six hazardous substances only if it comprises them less than MCV, since it is not possible to completely remove hazardous substances in EEE. It means, weight ratio of hazardous substance is included in weight of HM. As per RoHS Directive, the MCV of the six hazardous materials should be limited to 1000 ppm of homogenous material with cadmium limited to 100 ppm. If a circuit is made of different electronic components and materials, RoHS limits are applicable to all those components made of the same homogenous material. MCV of RoHS are shown in Table 1.

**Table 1. Maximum Concentration Value (MCV) of RoHS**

| Substances | Maximum Concentration Value of RoHS |
|---|---|
| Pb | 1,000 ppm |
| Hg | 1,000 ppm |
| Cd | 100 ppm |
| $Cr^{+6}$ | 1,000 ppm |
| PBBs (Polybrominated biphenyls) | 1,000 ppm |
| PBDEs (Polybrominated diphenyl ethers) | 1,000 ppm |

Samples were collected and prepared by assorting front and back parts as housing cover of used TV sets which were collected through EPR system. Sampling was focused on Company A and B as leading companies in South Korea dealing in domestic display industry and products of foreign brands. After identifying product information on wasted TV sets, they were assorted into front and back cover. Initially all metals except stranded copper wire and thin non magnetic cables were removed by magnet and hand sorting technique. Samples were grind to 2 mm size followed by gentle washing by nano pure distilled clean water and finally preserved for subsequent analysis (Spalvins, 2008). After quantifying the plastic types, material was reduced to the grain size <0.5 mm in consecutive steps by milling with a high performance cutting mill and sieving with different mesh sizes. Finally, 80 gram of the end fraction of 0.5 mm was ground to particle size <0.12 mm by an ultra centrifugal mill. Materials of display electronic products are regarded as general purpose Polystyrene (PS) composed of more than 90% High Impact Polystyrene (HIPS) grafted with rubber substances. Ten to twenty pieces of each sample manufactured in the same year of production were collected so as to minimize analytical error. Samples were analyzed by using EDX as RoHS test instrument. Results of the report conducted by proper filter for each sample interpreted through analysis of front cover (general purpose PS) are shown in Table 2 to 3.

After getting required grain size, the samples were subjected to close vessel microwave digestion. 0.5 g of the dried and ground sample was digested in a close vessel with 5 ml $HNO_3$ and 3 ml $H_2O_2$ followed by 3 ml HCl (26%). After digestion, contents were transferred into a 50 ml volumetric flask and the flask was made up

**Table 2. Interpretation of analysis report and EDX Set-up**

| Items | Filter | ppm | Sigma | Judgment | Time (Second) | DT (%) |
|---|---|---|---|---|---|---|
| Cd | MoNi | A mark of Final content in sample | Standard deviation: difference with practical value | OK- when threshold>contents | A time for measuring each item | A mark of extra time in % unit |
| Pb | Ag | | | | | |
| Hg | Ag | | | NG- when threshold<contents | | |
| Cr | Al | | | | | |
| Br | Ag | | | | | |

**Table 3. Analysis of front cover (General purpose PS) of Company B**

| Results | | | | | |
|---|---|---|---|---|---|
| **Method** | **EDX-RF** | | | | |
| **Sample preparation** | **None** | | | | |
| Element | Cadmium (Cd) | Lead (Pb) | Mercury (Hg) | Chromium (Cr) | Bromine (Br) |
| Threshold (ppm) | 50 | 200 | 700 | 700 | 300 |
| Content (ppm) | 235 | 46 | 49 | 47 | 1,022 |
| Std. Deviation (ppm) | 249 | 35 | 35 | 12 | 115 |
| Judgment | NG | OK | OK | OK | NG |

**Table 4. Average concentration of RoHS heavy metals (Unit:ppm)**

| Items | Cd | Pb | Hg | Cr | Br |
|---|---|---|---|---|---|
| RoHS allowance | 100 | 1,000 | 1,000 | 1,000 | 1,000 |
| Average concentration | 10.5 | 37.7 | 15.7 | 35.3 | 22,449.7 |

to the mark with distilled water. Finally the contents were shaken, filtered and made available for further analysis.

## RESULTS & DISCUSSION

The concentration in four categories, i.e., Cd, Pb, Hg and Cr showed lower contents than maximum allowable limit of RoHS (Table 4). The total bromine contents (T-Br, as an indicator allowing to estimate, if other brominated substances than the specifically analyzing brominated flame retardants occur in a plastic samples) were also analyzed. Although T-Br (22,449 ppm) exceeded the standard limit of RoHS, however, it is undeterminable whether T-Br exceeds the permitted concentration of RoHS or not, because brominated flame retardants (BFRs) affiliated with tetrabromobisphenol A (TBBPA), brom epoxy and halogen free are mainly used for housing cover of display product. As TBBPA concentration found in samples is most probably a consequence of its application in acrylonitrile butadiene styrene (ABS) plastic. This is supported by various studies that there are at least 75 different types of commercially available BFRs, of which 30-40 are widely used in EEE (Chen and Wang, 2009). These flame retardants are totally different components from PBBs and PBDEs. The fact that chemical compounds involving Br and brominated flame retardants classified into Level B substances in Class III are forbidden by RoHS Directive will have an effect on the future recycling industry. The Level B substances are harmful and hazardous substances for human health and global environment and still they are not regulated and anticipated to be prohibited by gradation in future.

RoHS heavy metal contents analyzed by respective manufacturer are shown in Fig. 1. In all the samples, level of lead content was found to lie below RoHS maximum concentration level of 1000 ppm. Nevertheless, concentration of Pb of company D and E out of 5 companies were higher to 2.1 and 4.3 times respectively, as compared to the average concentration of Pb of other companies. However, it can not be said that product from specific manufacturer has always higher contents of hazardous substance due to lack of number of samples taken (<10).

The results of analysis done with respect to production year are given in Fig.2. In case of all the four substances except T-Br, heavy metals in plastic can be regarded as contamination source included in the plastic as additional agents and colorant. Pb contents peaked in the products manufactured in 1998

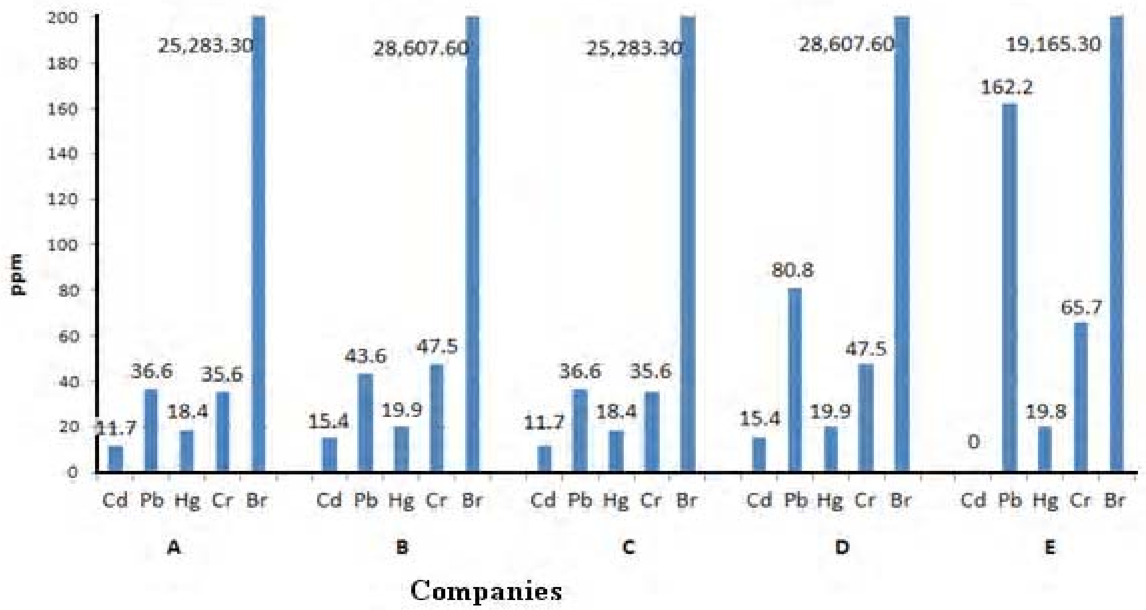


**Fig.1. Concentrations of RoHS materials with respect to manufacturers designated as A, B, C, D, & E**

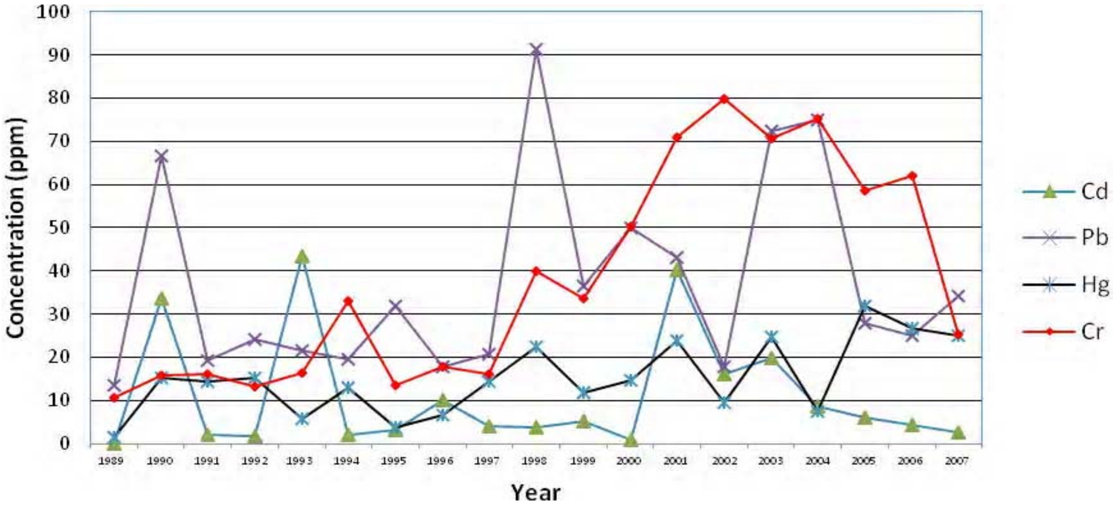


**Fig. 2. Concentrations of RoHS materials with respect to production year**

and Cr contents were peaked in the products of the year 2002. The contents of T-Br were gradually increased from 1989 to 2005 on account of using brominated flame retardants (Fig.3). In contrast, T-Br contents were remarkably decreased since 2005 by magnifying implementation of international environmental regulation regarding RoHS Directive. Moreover, it is considered that other flame retardants had been substituted for brominated flame retardants or they were used less as export to the European Union had been forbidden since July 2006. As per RoHS Directive, member states must ensure that from July 2006, newly marketed EEE does not contain above mentioned six hazardous substances higher than defined maximum concentration values for homogenous materials.

According to the result, concentrations of Cd, Pb and Cr were found more or less similar in both front and back cover of display product. However, concentrations of Hg and Br were significantly varied in both the parts. Especially, average concentration of Br was very high in back cover (Table 5). The concentration difference in these categories can be happened by features of the products; however, only sorting front cover and back cover might contribute for the diversity of recycling plan.

Over 90% of the plastic used in housing cover of display products was made of PS and PS-flame retardants (Fig. 4). However, various materials including ABS have been in frequent use in recent years. According to results, flame resistance PS contains higher Br than general purpose PS (Table 6).

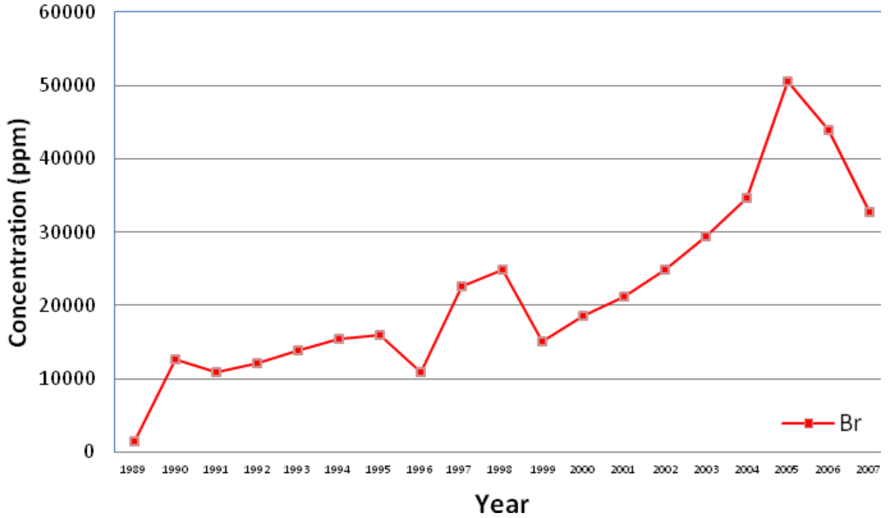


**Fig. 3. Total bromine concentration with respect to production year**

**Table 5. Concentration of RoHS heavy metals in each plastic part (Unit:ppm)**

| Items | Cd | Pb | Hg | Cr | Br |
|---|---|---|---|---|---|
| Front Cover | 9.7 | 37.5 | 9.6 | 33.5 | 12,563.3 |
| Back Cover | 11.2 | 37.9 | 21.8 | 37.2 | 32,336.2 |

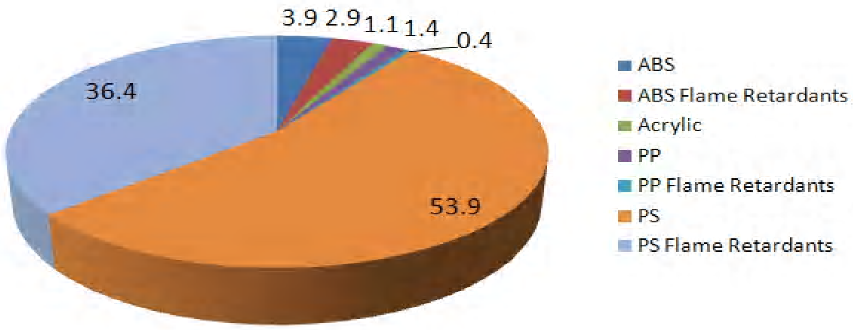


**Fig. 4. Distribution chart of plastic materials**

**Table 6. Concentration of RoHS heavy metals in various types of plastic (Unit:ppm)**

| Items | No of Samples | Cd | Pb | Hg | Cr | Br |
|---|---|---|---|---|---|---|
| ABS | 11 | 0.6 | 9.7 | 5.2 | 30.3 | 429.6 |
| ABS fireproof | 8 | 8.5 | 41.3 | 30.3 | 44.3 | 53,646.5 |
| P Arcylic | 3 | 0.0 | 11.3 | 2.7 | 6.0 | 20.3 |
| PP | 4 | 0.8 | 12.8 | 2.0 | 9.8 | 26.8 |
| PP fireproof | 1 | 9.0 | 22.0 | 44.0 | 66.0 | 52,299.0 |
| PS | 151 | 8.7 | 35.5 | 5.5 | 28.5 | 3,990.9 |
| PS fireproof | 102 | 15.0 | 45.6 | 31.4 | 46.8 | 50,950.4 |

Also, Hg in flame resistance PS is six times higher than in general purpose PS. It is mainly due to use of brominated flame retardant.

In total samples, peaks of each hazardous substance are shown in Fig. 5. The value of Br and Cd exceeded than allowable concentration. Lead was also found relatively higher. In addition to the presence of Pb bound to the plastics, higher concentration of Pb in the samples might be due to cross contamination during shredding process.

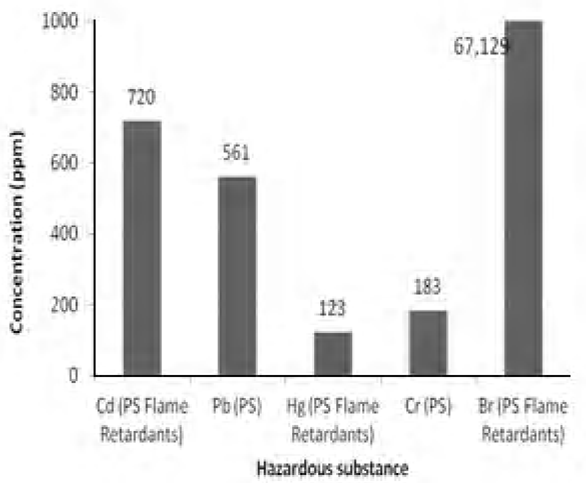


**Fig. 5. Peak analysis of hazardous substances**

## CONCLUSION

As the international environmental regulations dealing in manufacturing and export of electrical and electronic equipment are getting stringent day by day, this study examined the emission characteristics of hazardous substances and recycling effectiveness of WEEE plastics in South Korea. To maximize the recycling of waste plastic from display products in compliance with the Directive on RoHS, the use of brominated flame retardants in plastic and chromium plating in parts in synthetic resins should be restricted. Metal surface finishing such as coating and painting in high molecules synthetic resins should also be minimized since presence of hazardous substances within the allowance in the products can increase incentives for safe recycling practice. There is a need to develop and replace environment friendly materials and to essentially conduct an operation to remove hazardous substances with long term study period. Although the manufacturer oriented recovery-operation system of WEEE as EPR started in 2003 helped increase gradual expansion of recycling market, however it had played a marginal role. Enforcement of EPR system can be interpreted as a foundation for resource recycling society with such expectation that recycle obligation rate will gradually be increased.

## ACKNOWLEDGEMENT

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