

Research on the distribution of harmful substances in automotive products based on chemical quantitative

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Abstract. At present, China's automotive industry lacks standardized standards and testing methods for conducting harmful substance testing and evaluation of products. This article finely disassembled a passenger car model and conducted detection and analysis of harmful substances. More than 320000 materials were tested, involving 85 assembly components. This article studies six harmful substances in automotive materials, including lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, and polybrominated biphenyl ethers. The content of harmful substances and their distribution in different materials and components are analyzed. This article provides technical reference for conducting hazardous substance assessments in the automotive industry through data analysis. The harmful substance mainly contained in the studied automotive product is lead, which is mainly distributed in materials such as copper alloys, aluminum, steel, solder, plastics, etc. The content of mercury, cadmium, hexavalent chromium, polybrominated biphenyls, and polybrominated biphenyl ethers in automobiles is generally low.

1. Introduction

Since 2000, the European Union has successively issued "ELV Directive", "RRR Directive" and other mandatory regulations on the use of harmful substances in automotive products [1,2]. In 2015, China issued the "Management Requirements for Harmful Substances and Recyclability of Automobile", which requires domestic passenger cars to comply with relevant standards for lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, and polybrominated biphenyl ethers. With the release and implementation of policies, Chinese automotive companies have gradually begun to attach importance to harmful substance substitution technology and research and development work, and the content of harmful substances in products has been significantly reduced.

2. Research methods

This article provides a detailed disassembly and inspection of a vehicle model. The entire vehicle was disassembled to form 385 primary assembly components, covering more than 20000 material nodes. In addition, harmful substance content testing was conducted on each material node, and the quality was tested. Among them, the disassembly requirements shall be carried out in accordance with the GB/T 33460 standard. The testing method shall be carried out in accordance with the standards of QC/T 941, QC/T 942, QC/T 943, QC/T 944,

GB/T 23263, and QC/T 1131. The analysis of test results is based on GB/T 30512.

3. Current situation of hazardous substance management in domestic and foreign automobiles

3.1. Current situation of EU management

The European Commission issued a directive on scrapped vehicles in 2000, requiring the implementation of hazardous substance and recycling management for M1 and N1 category vehicles, as well as three wheeled motor vehicles and their components and materials, except for three wheeled motorcycles. In terms of harmful substances, the EU stipulates that member states should control and reduce the use of four harmful substances in cars, including lead, mercury, cadmium, hexavalent chromium, etc., and should promote recycling and avoid discarding hazardous waste to prevent such substances from being released into the environment.

3.2. Current management situation in South Korea

The Resource Recycling Agency of the South Korean Ministry of Environment formulated and promulgated the Resource Recycling and Utilization Act for Electrical and Electronic Products and Vehicles (referred to as the Recycling Act) on April 27, 2007, and officially implemented it on January 1, 2008. This bill is the first

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law in South Korea specifically aimed at the recycling and reuse of electronic and electrical products and automotive products. It draws on the advanced aspects of the European Union's WEEE, RoHS, and ELV directives and is the main law in South Korea for implementing the management of hazardous substances and recycling in automobiles. The bill strictly limits the content of four harmful substances, including lead, mercury, cadmium, and hexavalent chromium, in automotive products, and proposes that automobile manufacturers/importers should disclose whether they comply with the restrictions on the use of harmful substances.

3.3. Current Management Situation in China

In 2015, China issued the "Management Requirements for Harmful Substances and Recyclability of Automobile", which requires domestic passenger cars to comply with relevant standards for lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, and polybrominated biphenyl ethers. With the continuous implementation of ELV management in our country, the industry has established an ELV control mechanism of "enterprise declaration compliance verification result disclosure", and has issued thirteen batches of "List of Compliance with the Management Requirements for Harmful Substances and Recyclable Utilization of Vehicles" for With the implementation of ELV management policies, the use of six controlled harmful substances, including lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, and polybrominated biphenyl ethers, has been significantly reduced. Among them, the average usage of lead (excluding lead-acid batteries) has been reduced by about half from 220 grams per vehicle (2015), and the cumulative reduction in lead usage has reached more than 10000 tons.

4. Results and Analysis

4.1. Classification analysis of automotive product materials

The materials used in automobiles can be roughly divided into two categories: metallic materials and non-metallic materials. Metal materials include steel plate, cast iron and other heavy metal materials, aluminum, magnesium, titanium and other light metals and their alloy materials, foam metal and so on. Non metallic materials include polymers, glass, plastics, rubber, etc.

The quality comparison of different materials in the automotive products analyzed in this article is shown in Figure 1. Among them, the metal mass is the largest, at 1034.14kg; Next are plastic and polymer materials, with masses of 164.38kg and 150.75kg respectively; Rubber and glass materials are relatively few, with masses of 33.66kg and 32.65kg respectively; The total weight of other materials is 4.68kg.

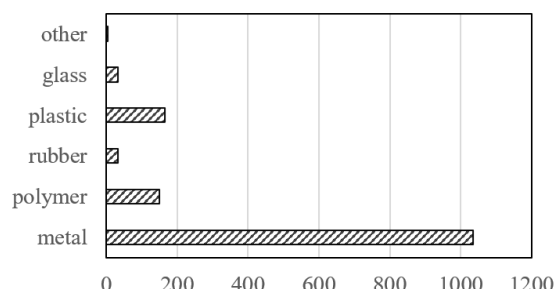


Figure 1. Classification analysis diagram of automotive materials.

4.2. Analysis of lead distribution in automotive products

After lead and its compounds enter the human body, they may deposit in the body, causing damage to the nervous, hematopoietic, digestive, renal, cardiovascular, endocrine and other systems, leading to lead poisoning[3]. Lead in automotive products is often used in lead-acid batteries, cable sheaths, etc.

4.2.1 Distribution of lead in the entire vehicle

The distribution of lead in the entire vehicle is shown in Figure 2. Out of more than 20000 testing materials in the entire vehicle, there are a total of 813 points containing lead materials. The proportion of sites with lead content exceeding 10000mg/kg is 15.74%, mainly composed of copper alloys, aluminum materials, solder materials, etc., mainly distributed in battery assemblies and electronic and electrical equipment (ceramics), all of which are exempted components and materials. Among them, the aluminum lead content in the battery electrode plate is the highest, with multiple points exceeding 900000mg/kg. The sites with lead content ranging from 1000 to 5000mg/kg have the highest proportion, accounting for 56.58% (See Figure 3 for details). Mainly distributed in steel and electronic and electrical equipment (ceramics). Most of them are exempted materials and components, but after chemical quantitative analysis, the lead content of three plastic parts exceeds 1000mg/kg, which may not meet relevant standards.

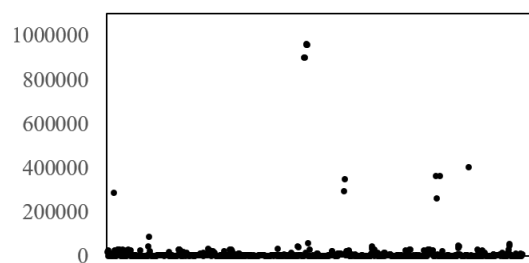


Figure 2. Distribution diagram of lead in the entire vehicle

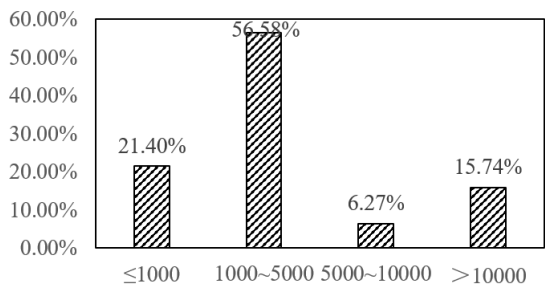


Figure 3. Diagram of the proportion of materials with different lead contents

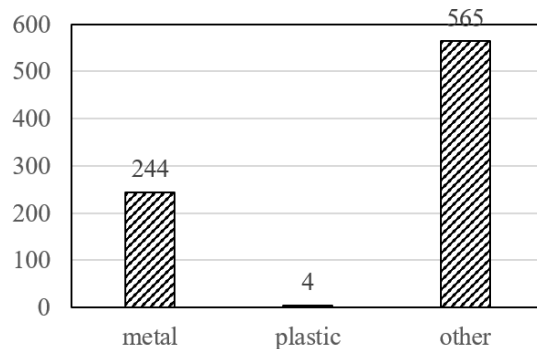


Figure 4. Distribution diagram of lead in different materials

4.2.2 Distribution of lead in different types of materials

From the distribution of lead in different materials, as shown in Figure 4. Plastic contains the least amount of lead, with only 4 locations detecting the presence of lead; Next is metallic materials, with a total of 244 lead containing sites. There are 565 lead containing sites in other materials. Other materials include electrolytic paper, electronic and electrical equipment, etc.

By analyzing the lead content of different types of materials, as shown in Table 1. The main lead containing materials in the entire vehicle are copper alloy, aluminum, coating, steel, solder, and plastic. From the quantity of materials containing lead, copper alloy has the highest quantity, at 99; Next are aluminum, coatings, and steel, with the least amount of plastic containing lead. From the perspective of lead content, solder has the highest lead content, with a maximum value of 91965mg/kg and an average value of 74024mg/kg; Next is copper alloy, with a maximum value of 91965mg/kg, an average value of 33290mg/kg, and an average value of 18922mg/kg; The lowest lead content is in the coating, with a maximum value of 628mg/kg and an average value of 168mg/kg.

Table 1 Distribution of lead in different materials

Material type	Quantity of lead containing materials (pieces)	Maximum value (mg/kg)	Minimum value (mg/kg)	Average value (mg/kg)
Soldering	12	91965	67576	74024
Coating	34	628	13	168
Steels	31	3456	16	356
Aluminum	79	2467	17	180
Plastic	4	2600	320	1532
Copper Alloy	99	33290	7313	18922

By analyzing the proportion of materials with different lead contents in different intervals, as shown in Figure 5. It can be seen that the lead content of solder is generally higher, all higher than 10000mg/kg; The lead content in the coating is relatively low, all below

1000mg/kg. The lead content of most copper alloys ranges from 5000 to 10000mg/kg; The lead content of most plastics ranges from 1000 to 5000mg/kg; Most aluminum materials are below 1000mg/kg, while a few materials are between 1000-5000mg/kg.

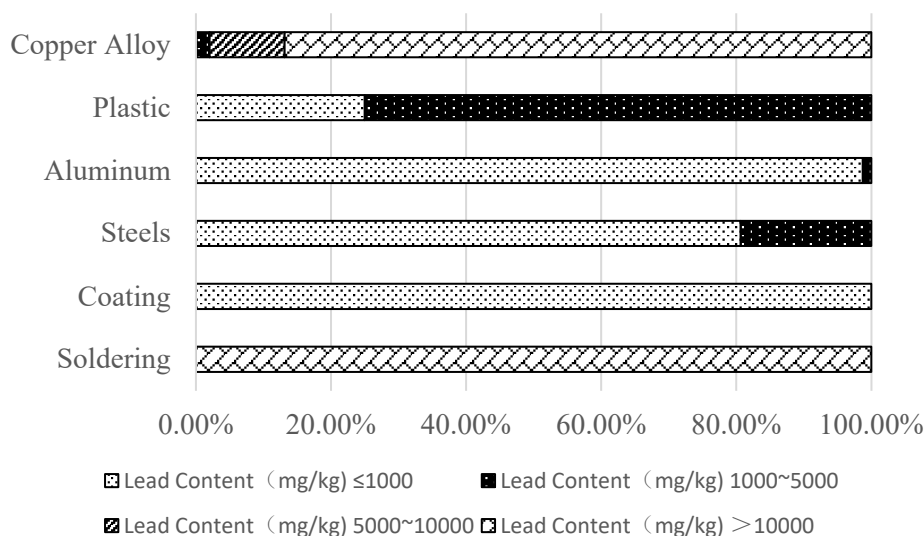


Figure 5. Distribution of Material Types with Different Lead Content

4.3. Analysis of mercury distribution in automotive products

Oral, inhalation, or exposure to mercury can cause brain and liver damage. Mercury can accumulate in living organisms and is easily absorbed by the skin, respiratory tract, and digestive tract[4]. Most harmful substances such as mercury exist in the form of compounds in the interior of vehicles, especially in seats, gearshift handles, instrument panels, and enamel materials. Some car paint on the surface of the car also contains mercury.

According to statistics on the distribution of mercury in the entire vehicle, As shown in Figure 6. Only three points were detected for the presence of mercury, with concentrations of 1620mg/kg, 2381mg/kg, and 2726mg/kg, respectively. Mercury containing materials are mainly distributed on the tungsten wire in license plate lamps. Its material type belongs to electronic and electrical equipment and is an exempted component.

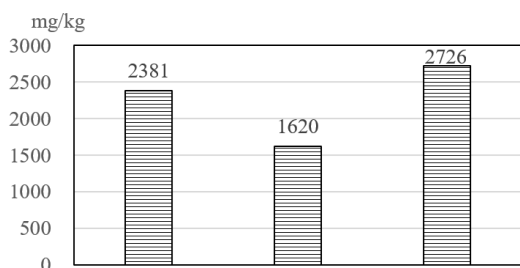


Figure 6. Distribution of Mercury in Different Materials

4.4. Analysis of cadmium distribution in automotive products

When the environment is contaminated with cadmium, cadmium can accumulate in organisms and enter the human body through the food chain, causing chronic poisoning[5]. Cadmium coatings can enhance the corrosion resistance of metals such as steel, brass, and aluminum, and can be used as corrosion protection coatings for screws, fastening devices, vehicle chassis, and other structural components in industries such as electronics and automotive manufacturing.

According to the analysis of the distribution of cadmium in the entire vehicle, the results are shown in Figure 7. In the entire vehicle, a total of 13 material testing points detected the presence of cadmium. The cadmium content in the entire vehicle is generally low. The material with the highest cadmium content is electrolytic paper, which is 45mg/kg. Cadmium is widely distributed in metal materials, such as copper alloys, aluminum materials, coatings, etc. The main components involved include electrodes, metal washers, and camera shells.

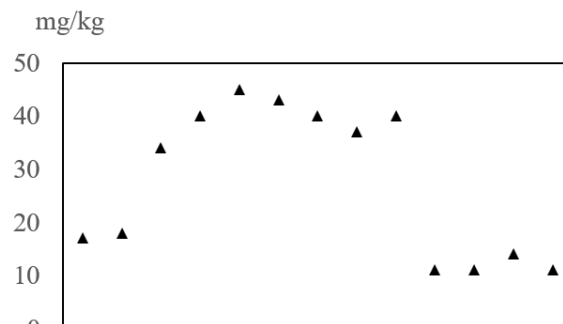


Figure 7. Distribution diagram of cadmium in different materials

4.5. Analysis of the Distribution of Hexavalent Chromium in Automotive Products

Hexavalent chromium may cause skin irritation, tissue and cell damage, and even digestive system damage to the human body[6,7]. The industrial uses of hexavalent chromium compounds include chromate pigments in dyes, paints, inks, and plastics, chromates added as preservatives to paints, primers, and other surface coatings, and chromates electroplated on metal components to provide decorative or protective coatings.

The distribution of total chromium in automotive products was analyzed using XRF instruments, and the results are shown in Figure 8. The entire vehicle has 20000 points containing chromium, with a focus on materials such as metal, plastic, and rubber. But these chromium elements contain trivalent chromium and hexavalent chromium. Through further chemical quantitative analysis, the results showed that the entire vehicle did not contain hexavalent chromium.

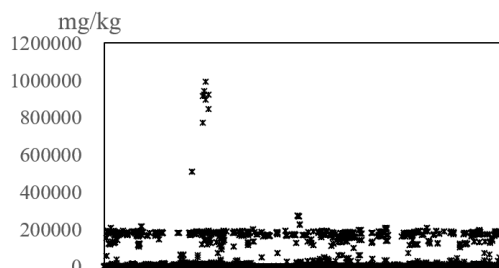


Figure 8. Distribution of Total Chromium in Different Materials

4.6. Analysis of the distribution of brominated flame retardants in automotive products

Polybrominated diphenyl ethers and polybrominated biphenyls, their toxicity mainly affects the human endocrine system and fetal growth. When plastics containing such flame retardants are overheated or incinerated, they will produce bromodiphenyldioxins or furans, which are carcinogens and can cause serious and widespread pollution, including soil, water, and air. Brominated flame retardants can be added to composite materials during the manufacturing process of automotive products to improve their fire resistance.

Through chemical quantitative detection and analysis, it was found that the entire vehicle does not contain

polybrominated biphenyls (PBBs), but a small portion of materials contain polybrominated biphenyl ethers (PBDEs), as shown in Table 2. The polybrominated diphenyl ethers (PBDEs) contained in the entire vehicle are mainly nine brominated diphenyl ethers and ten brominated diphenyl ethers, and are mainly distributed in materials such as plastics and rubber, involving components such as shock absorbers and plastic shells.

Table 2 Distribution of Polybrominated Diphenyl Ethers in Different Materials

No.	Component Name	PBDEs (mg/kg)	Material type
1	Shock absorber rubber ring	Nine bromodiphenyl ether: 768	rubber
		Decabromodiphenyl ether: 17098 (exempted)	
2	plastic shell	258	plastics
3	plastic shell	255	plastics
4	plastic shell	256	plastics
5	rubber block	Nine bromodiphenyl ether: 840	rubber
		Decabromodiphenyl ether: 15847 (exempted)	

5. conclusion

This article provides a detailed disassembly and inspection of a vehicle model, involving 385 primary assembly components and over 20000 materials. This study first conducted initial screening using XRF instruments, and then determined the accurate content of lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, and polybrominated biphenyl ethers through chemical quantitative analysis. Meanwhile, this article also analyzed the distribution of harmful substances in different materials. The following conclusions can be drawn from this article:

1) The harmful substance lead is widely distributed in automotive materials. A total of 813 materials in the vehicle contain lead, which is mainly distributed in components or materials such as batteries, electronic and electrical equipment, steel, and aluminum.

2) Lead in automotive materials is mainly distributed in electronic and electrical equipment. Metal materials have the second highest lead content. Lead content is relatively low in plastics.

3) Mercury and cadmium are less distributed in automotive materials. The automotive products in this study do not contain hexavalent chromium.

4) In this inspection, no polybrominated biphenyls (PBBs) were found in the car, and only a small portion of the materials contained polybrominated biphenyl ethers (PBDEs), mainly nine brominated biphenyl ethers and ten brominated biphenyl ethers..

In summary, the automotive products studied and tested in this article generally contain harmful substances such as lead, mercury, and cadmium, but all of them meet the standard requirements. It can be seen that with

the release and implementation of policies related to the management of harmful substances in automotive products in China, the harmful substances in automotive products have been effectively controlled.

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