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To cite this article: Meng Hou et al 2019 IOP Conf. Ser.: Earth Environ. Sci. 227 052046

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Research on application mechanism of cadmium in new energy vehicle charging group

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Abstract. The cadmium is seriously harmful to the environment and human health, which has been brought in the controlled list of prohibited substances. This paper analyses the application, distribution and content of cadmium in the charging components of new energy vehicles, and considers that the cadmium is in the form of controlled elements in automotive products, and its main uses in new automotive products have mature substitution and reduction technologies, which can achieve all unintentional addition. However, the recent cadmium event of Volkswagen charging component indicates that there is still a long way to walk before the consistency management of automotive products, and it will be inevitable that ELV management will tilt toward the after-the-fact supervision.

1. Introduction
Volkswagen may be forced to recall 124,000 pure electric and hybrid vehicles in the future due to carcinogenic cadmium found in the charging group battery this year. It is reported that the charging group of the battery mounted on its new energy vehicle contains an average of 0.008g cadmium. This report has attracted close attention from industry and consumers, and heavy metal cadmium has become the focus once again.

Being highly toxic, Cadmium is ranked in the sixth place by the American Agency for Toxic Substances and Disease Registry (ATSDR) as a toxic and harmful substance to human health [1]. Contaminants containing cadmium, once entering into the soil in various ways, have strong chemical activity in soil, which can be easily absorbed by plants and enter into the food chain, thereby threaten human health. The main hazards of cadmium to human health are connective tissue damage, reproductive system dysfunction, kidney damage, teratogenesis and breast cancer, etc. [2].

As listed in ELV Directive (2000/53/EC) issued by European Union (EU) in September 2000, cadmium is one of the four heavy metals under control, and it is banned that no presence of cadmium in vehicles shall enter into the market after 1 July 2003. In addition, China has listed cadmium as one of the six hazardous substances in the control of automotive products in "Management Requirements for Harmful Substances and Recyclable Utilization Rate of Automobile" implemented on January 1, 2016, with a limit value of less than 0.01%, except for spare Ni-Cd batteries for electric vehicles.

2. Application of cadmium
Cadmium is of various purposes and distinct complicated existing forms, such as metal cadmium, cadmium oxide, cadmium sulfide, and cadmium chromate, etc. In automotive products, cadmium is
mainly involved in the following situations: First, nickel-cadmium battery; second, heat stabilizer; third, contact material; fourth, aurora yellow.

The positive plate of nickel-cadmium battery is made of active materials composed of nickel oxide powder and graphite powder, among which graphite does not participate in a chemical reaction and mainly functions as the conductivity enhancing. The anode plate is an active material composed of cadmium oxide powder and iron oxide powder. The main function of iron oxide powder is to increase diffusivity of cadmium oxide powder, prevent agglomeration and increase plate capacity. Active substances on the positive and negative plates are respectively wrapped in perforated steel strips and pressurized to form. The polar plates are isolated by alkali-resistant rigid rubber insulating rods or porous PVC corrugated plates, and the electrolyte is usually potassium hydroxide solution. Nickel-cadmium battery is one kind of DC power supply battery, which is an ideal DC battery widely used in the electric vehicle power supply with the advantages of low internal resistance, fast charging, high current load, stable discharge voltage, economical and durable features and was widely adopted as the power supply of electrical vehicles. Its main shortcomings are that it has a "memory effect" that reduces the battery capacity; in addition, as cadmium is toxic and seriously harmful to the environment and human health, nickel-cadmium batteries have been basically replaced by nickel-hydrogen batteries.

Heat stabilizer is one of the important categories of plastics processing agents, which is widely applied. Polyvinyl chloride (PVC) is considered as one of the most versatile plastics because of its excellent properties, with the main disadvantage of poor thermal stability. The thermal stabilizer is a necessary auxiliary reagent in its shaping processing. Ba-Cd composite thermal stabilizer is an excellent plastic stabilizer, which has been widely used in the manufacture of PVC products. Its main advantages are as follows: (1) The liquid Ba-Cd composite stabilizer contains oleic acids of a higher unsaturated fatty acid structure, which can improve the low-temperature resistance of PVC plastics; (2) Adding Ba-Cd composite stabilizer is of a short process, with simple equipment, convenient operation, and wide source of raw materials; (3) Adding liquid Ba-Cd composite stabilizer can mix the resin evenly, and keep a safe, free-of-dust utilization at a low cost; (4) Ba-Cd composite stabilizer can reduce the processing temperature of PVC plastics. However, due to the increasingly stringent environmental requirements, cadmium-free thermal stabilizer has replaced cadmium-containing stabilizers, such as barium-zinc composite stabilizers, organotin stabilizers, and mixed metal stabilizers, etc.

Most of the early contact materials used in automobile products in China are pure silver or silver-copper alloys, or even platinum or palladium alloys for some high-end vehicles. Silver-copper contact material has good electrical conductivity and relatively low contact voltage drop, despite some defects, such as directional transfer under the action of DC arc, adhesion or even permanent welding occurred under instantaneous high current. In addition, contact parts made of the material are of large volume and high silver content, resulting in inconvenience of installation and use and high cost. Meanwhile, platinum and palladium alloys are precious metals, expensive and unsuitable for wide application. Therefore, these two materials are not suitable for the rapid development of the automotive industry of China, which are gradually replaced by silver nickel and silver cadmium oxide materials. Silver cadmium oxide (AgCdO) electrical contact material has been widely used in low voltage electrical apparatus under 1500V since the 1950s because of its excellent resistance to arc erosion, welding and low contact resistance, which is called "universal contact" [3] and is a commonly used contact material for relays [4]. However, cadmium is a toxic element. Cadmium vapor produced by the electric arc is emitted into automobiles when switching electric switches, which will not only pollute the environment, but also endanger the health of passengers in automobiles. As the increasingly stringent environmental requirements, silver cadmium oxide contact materials can not meet the requirements of laws, silver tin oxide materials have come into being. The contact material uses non-toxic and harmless tin element instead of cadmium, and reduces contact size and contact spacing on basis of its excellent performance of arc corrosion resistance, weld resistance, and high electrical life, etc., thus making the product smaller, more compact in structure, and becoming an ideal environmental friendly contact material, which is the most popular contact material for automotive electrical products. In
addition to silver tin oxide, there are silver zinc oxide, silver beryllium oxide [5] and other contact materials, with relatively small application scope.

Pigments are an indispensable part of plastics, fiber, coatings and other industries. Cadmium yellow is a yellow inorganic pigment mainly composed of cadmium sulfide or solid solution of cadmium sulfide and zinc sulfide, with its color varying from yellow to light yellow [6] as the increase of solid solution volume of zinc sulfide. At present, besides cadmium yellow, there is molybdenum yellow without cadmium and inorganic pigments, which are adopted as substitutes for cadmium yellow in plastics, fibers and coatings.

The introduction of cadmium element, besides the above purposes added deliberately, may be used as impurities in metal materials, such as zinc alloy, aluminum alloy, copper alloy, solder, etc., especially in zinc alloy. As zinc and cadmium ores are associated minerals, cadmium is relatively common in zinc alloy; cadmium element is mostly harmful, it is strictly controlled at a relatively low content.

3. Cadmium content in charging group of new energy vehicles

In view of the Volkswagen charging group cadmium-containing issue, we have investigated and studied the application of cadmium in charging groups from multiple aspects. The main distribution of cadmium in vehicle-mounted charging group is shown in Table 1.

| No. | Component Names | No. | Component Names |
|-----|-----------------|-----|-----------------|
| 1   | Zinc plated layer on fixed rack of vehicle-mounted charging group control panel | 14  | Pre-charging resistance line of front drive pre-charging contactor |
| 2   | Tin plated layer on a jumper of vehicle-mounted charging group jumper | 15  | Charging port cover inhaul cable |
| 3   | Vehicle mounted charging group solder | 16  | Charging group pin |
| 4   | Vehicle mounted charging group electrical components | 17  | Vehicle mounted charging group radiator |
| 5   | Charging gun terminal | 18  | Vehicle mounted charging group cable waterproof joint |
| 6   | Charging gun cable sheath | 19  | Zinc tin plated layer on the capacitor of vehicle charging group |
| 7   | Double elbow charging linear cable core | 20  | Vehicle charging group plug-in thermistor - NTC line |
| 8   | Zinc plated layer on the buckle of double elbow charging linear cable shelf cover | 21  | Charging plug - silver plated layer |
| 9   | Charging group box capacitor | 22  | Charging plug lock - solder |
| 10  | Charging group relay contact | 23  | Charging group lead |
| 11  | Reed spring socket wiring of AC charging socket | 24  | Zinc alloy lock core of charging port |
| 12  | DC charging port copper strand | 25  | Charging group bearing |
| 13  | AC vehicle charging socket assembly | 26  | Charging gun aluminum alloy mechanism parts |

Cadmium-related components are widely used, mainly concentrating in coatings, electrical components, wiring cores, joints, solders, contacts and a small number of structural components etc. in the existing forms of metal elements and compounds, mostly including metal cadmium, cadmium oxide, cadmium red, and cadmium yellow. The main types of materials involving cadmium are shown in Table 2. Copper alloy, Zinc alloy, Solder, Silver cadmium alloy and Zinc-Tin coating are the main types of materials involving cadmium, which should be paid attention to.
Table 2. Cadmium-containing material.

| Material Grade | Material Type   | Material Grade | Material Type   | Material Grade | Material Type   |
|----------------|----------------|----------------|----------------|----------------|----------------|
| C3602          | Copper alloy   | Pb97.5Ag1.5Sn1 | Solder         | Z56900         | Coating        |
| C3604          | Copper alloy   | Sn63Pb37       | Solder         | Z12003         | Coating        |
| C1011          | Copper alloy   | Sn96.5Ag3Cu0.5 | Solder         | 50Zn/50Sn      | Coating        |
| C1100          | Copper alloy   | Sn96Ag3Cu1     | Solder         | 6061-T6        | Aluminum alloy |
| C3604          | Copper alloy   | Sn97Ag3        | Solder         | ADC12          | Aluminum alloy |
| Cu-ETP1        | Copper alloy   | Sn99.3Cu0.7    | Solder         | AL6063         | Aluminum alloy |
| CW003A         | Copper alloy   | Sn99Cu0.7Ag0.3 | Solder         | AgCdO          | Silver cadmium |
| H59            | Copper alloy   | Sn99Cu1        | Solder         | AG-41A         | Zinc alloy     |
| H62            | Copper alloy   | BVAu-2         | Solder         | YZZnAl4A       | Zinc alloy     |
| H65            | Copper alloy   | Ag72Cu-780     | Solder         | YZZnAl4Cu3     | Zinc alloy     |
| H70            | Copper alloy   | Pb90Sn10       | Solder         | ZnAl4Cu1       | Zinc alloy     |
| Phosphor       | Copper alloy   | Pb92Sn5Ag      | Solder         | ZZnAl4Cu3Y     | Zinc alloy     |
| bronze         | Oxygen free    | Pb93Sn5Ag2     | Solder         | ZZnALD4-3      | Zinc alloy     |
| Oxygen free    | Copper alloy   | Pb93Sn5Ag2     | Solder         | ZZnALD4-3      | Zinc alloy     |
| TPE            | Polymer        |                |                |                |                |

For the cadmium content of the charging group assembly, we analyzed 15 types of charging group products from 15 domestic enterprises, and summarized each cadmium content. It was found that the cadmium content of all charging groups met the 0.01% limit value requirement. As calculated, the result of the total cadmium content in charging groups is shown in Figure 1 below.

Figure 1. Cadmium content in charging group assembly.

As indicated in Figure 1, cadmium contents of 15 types of charging groups are between 0.000002g and 0.002870g, with an average content of about 0.000637g. However, the range of cadmium content is large, and the maximum value can be over 1000 times as much as the minimum value.

Compared with the exposure of cadmium contents of Volkswagen new energy vehicle charging group, the average cadmium content of 15 products in China is only 0.000637g, while the exposed cadmium content of Volkswagen charging group is 0.008g, 12.6 times of the average cadmium content of the 15 models in China, 2.8 times of the maximum value. The cadmium content is at an abnormal level. In addition to the metal materials deemed as impurities, the main cadmium additives include contact materials, polymer heat stabilizers and cadmium yellow. According to our investigation, cadmium yellow has not been found, while silver cadmium oxide and cadmium-containing heat stabilizers have been used in charging group.
The main component of cadmium yellow is CdS or Cd/ZnS. The deeper the yellow color, the higher the CdS content. The ratio of Cd element content in dark yellow is about 77.8%. The use of this pigment will cause the cadmium content in the material to exceed the limit value. According to statistics, it is indeed possible to use yellow cable insulation in new energy vehicle charging components, which is one of the possibilities for cadmium exceeding the limit value. The contact switch is a commonly used component of electrical equipment. In the silver cadmium oxide contact material, the cadmium content is about 13.1%-20.8%. Although silver cadmium oxide contact materials have withdrawn from automotive products in accordance with regulatory requirements, they are still used in other fields. This time, the cadmium event of Volkswagen's charging group is extremely likely to be misused using silver cadmium oxide contact switch materials.

Therefore, attention should be paid to the use of silver cadmium oxide contact materials and heat stabilizers containing cadmium, for the control of cadmium element in the charging group.

4. Conclusions

Through the analysis of the application of cadmium, distribution in automotive products, and content data, in combination with the Volkswagen cadmium incident, this paper made a comprehensive assessment on the cadmium content of the new energy vehicle charging components, and believes that:

1) In the current automobile industry, the cadmium utilization is strictly regulated (there is no cadmium exemption for new automobile products), and the cadmium alternative technology is relatively mature. Under such condition, cadmium exists in automobile products as a largely controlled element in forms of copper alloy, aluminum alloy, zinc alloy and most solders, etc. Covering a relatively limited content in these materials, cadmium mainly involves micro/small components, so the overall content is not high.

2) As shown by Volkswagen charging components cadmium incident, although cadmium should not exceed limits or volume in automobile products from aspects of regulation requirements and technical substitution, the production consistency issue is still the key to the compliance of automobile products. Therefore, the only effective way to strengthen the ex-factory supervision and carry out the ELV consistency inspection of automotive products is to ensure the consistency of automotive products and compliance with ELV regulations.

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