November, 2007

Evidence of recycling of lead battery waste into highly leaded jewelry

Jeffrey D Weidenhamer, *Ashland University*
Micheal L Clement, *Ashland University*

Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Chemosphere xxx (2007) xxx–xxx
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

Short Communication

Evidence of recycling of lead battery waste into highly leaded jewelry

Jeffrey D. Weidenhamer *, Michael L. Clement

Q2 *Department of Chemistry, Ashland University, 401 College Avenue, Ashland, OH 44805, USA*

Received 3 April 2007; received in revised form 30 May 2007; accepted 1 June 2007

Abstract

Inexpensive highly leaded jewelry, much of it imported from China, remains widely available in the United States. The source materials for these items are unknown. Due to the low cost of much of this trinket jewelry, it seems likely that scrap materials may be used in their manufacture. Thirty-nine jewelry items previously determined to contain 90% or more lead by weight were analyzed for antimony content. The average antimony content of these thirty-nine items was 3.0%. The range of antimony content in the samples was from 0.3% to 6.2% antimony by weight, with twenty-seven of the samples in the range of 2–4% antimony by weight. By comparison, battery lead standard reference material obtained from the US National Institute of Standards and Technology contains 2.95% antimony by weight. While the evidence is circumstantial, the similarity in composition of these samples to battery lead is striking and supports the hypothesis that some battery lead is being recycled into highly leaded jewelry items. These results suggest that the recycling of this waste in China needs to be investigated, as the use of lead battery waste as a source material for children's jewelry poses a clear threat to children's health.

Keywords: Lead; Jewelry; Neurotoxicity; Children's health; Lead-acid battery waste

1. Introduction

The US Consumer Product Safety Commission (CPSC) is currently considering a ban on children's jewelry containing more than 0.06% lead by weight (US CPSC, 2007). This ban would replace the agency's current interim enforcement standard (2005) which is defined both in terms of lead content (lead must be less than or equal to 0.06%, or 600 ppm) and accessibility of lead to dilute acid leaching designed to simulate dissolution in the digestive tract (total accessible lead must be less than or equal to 175 μg). This proposed ban follows the death from lead poisoning of a four-year-old child who swallowed a heart-shaped charm on a Reebok charm bracelet that contained 99% lead by weight (Associated Press, 2006; CDC, 2006). Inexpensive highly leaded jewelry, often imported from China, remains widely available in the United States despite the current interim enforcement policy (Maas et al., 2005; Weidenhamer and Clement, 2007a).

The source materials for these jewelry items are unknown. Due to the low cost of this jewelry, it seems likely that scrap materials may be used in their manufacture. In the case of the Reebok bracelet, analyses of multiple bracelet samples found lead content of the charms ranging from 0.07% to 99.1% by weight, a result which suggests opportunistic use of scrap source materials (CDC, 2006). One potential source of scrap lead is the large quantity of e-waste that is exported from the United States to a number of poorer nations, including China. We recently analyzed sixteen jewelry items previously determined to contain 20–80% lead by weight for lead, tin and copper, and found evidence that several of these items had compositions suggestive of a solder-based source material (Weidenhamer and Clement, 2007b).

However, it is unlikely that electronic solders with original concentrations of approximately 40% lead by weight

* Corresponding author. Tel.: +1 419 289 5281; fax: +1 419 289 5283.
E-mail address: jweiden@ashland.edu (J.D. Weidenhamer).

0045-6535/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.chemosphere.2007.06.005

would be the source materials for the significant number of very heavily leaded samples from our original dataset (Weidenhamer and Clement, 2007) which contained more than 80% lead by weight. The biggest use of lead is in the manufacture of lead-acid automobile batteries (Ahmed, 1996). In China, growth in the transportation sector is creating a growing demand for lead-acid batteries and presumably, the recycling of used batteries. However, the several kg of lead in one used battery could be used to produce many highly leaded jewelry items, and the diversion of a small fraction of recycled lead-acid batteries to the production of jewelry could thus provide a large quantity of fairly inexpensive, highly leaded scrap lead for jewelry production. Automotive battery lead alloys typically contain 1.5–4.5% antimony by weight (Prengaman, 2006). The objective of this study was to determine whether recycled battery lead is a possible source material for highly lead jewelry items, by analyzing thirty-nine jewelry items previously determined to contain 90% or more lead by weight (Weidenhamer and Clement, 2007a) for antimony content.

2. Materials and methods

2.1. Samples

Information on purchase and handling of the jewelry samples has been previously described (Weidenhamer and Clement, 2007a). The samples identified as containing 90% or more lead by weight were selected for analysis of antimony content. Except for one item, a hair pin manufactured in South Korea, all other items were marked as Chinese imports.

2.2. Chemical analyses

Methods followed those of Maas et al. (2005), and are detailed in Weidenhamer and Clement, 2007a. Following digestion of small pieces of each item (0.1–0.2 g) in 50% (v/v) trace metal grade nitric acid and subsequent dilution, samples were analyzed by flame atomic absorption spectrophotometry (SpectrAA 220 FS equipped with the sample introduction pump system SIPS-20; Varian, Walnut Creek, CA, USA). Analytical conditions for Pb have previously been reported (Weidenhamer and Clement, 2007a), and for Sb were 217.6 nm using an air-acetylene flame. Quality assurance and quality control were tested by processing blank samples, fortified laboratory blanks, and standard reference material (SRM; battery lead SRM c2415; National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA). In addition, a duplicate was run for every tenth jewelry sample. It was not found necessary to apply the method of standard additions to resolve matrix effects. Concentrations obtained for the SRM were (values for relative standard deviation in parentheses) 98.9% (±2.97) of the certificate value for lead, and 101.4% (±7.16) of the certificate value for antimony. The certified total of all non-lead components of the battery lead SRM is 3.64% by weight, leaving a balance of 96.36% lead by weight in the SRM.

3. Results and discussion

Antimony and lead content of the thirty-nine items tested is shown in Table 1. Antimony content ranged from 0.3% to 6.2% by weight in these samples, and averaged 3.0%. Twenty-seven of the thirty-nine samples had an antimony content of 2.0–4.0% by weight. By comparison, the NIST battery lead SRM contains 2.95% antimony by weight. The similarity in composition of many of these items to the lead-antimony alloys used in automotive batteries is striking, and suggests that recycling of battery lead

Table 1
Antimony and lead content (% by weight) of highly leaded jewelry items

Sample no.	Jewelry type[a]	% Sb	% Pb	Total Sb + Pb
1	B	6.2	90.7	97.8
2	B	6.0	92.2	98.2
3	N	5.6	90.3	95.9
4	K	5.6	90.8	96.4
5	H	4.3	91.3	95.5
6	K	4.0	97.5	102.0
7	K	3.8	92.8	96.6
8	K	3.7	90.9	94.6
9	R	3.6	90.0	93.6
10	B	3.6	94.4	97.9
11	B	3.2	90.6	93.8
12	N	3.2	90.5	94.2
13	B	3.2	93.5	96.7
14	K	3.2	92.5	95.7
15	K	3.1	93.1	96.2
16	B	3.0	92.0	95.0
17	B	2.9	93.5	96.4
18	P	2.9	90.6	93.5
19	P	2.9	100.6	103.8
20	K	2.9	95.4	98.7
21	P	2.9	94.6	97.5
22	B	2.8	95.6	98.5
23	K	2.8	94.2	97.0
24	K	2.8	95.3	98.1
25	B	2.7	96.5	99.2
26	B	2.6	93.3	95.9
27	E	2.6	91.8	94.4
28	B	2.6	92.9	95.5
29	E	2.5	91.3	93.9
30	K	2.4	95.7	98.1
31	E	2.4	90.8	93.2
32	N	2.0	93.7	95.7
33	E	1.8	90.1	91.9
34	K	1.8	93.6	95.3
35	K	1.7	91.5	93.2
36	B	1.6	91.2	92.8
37	K	1.4	100.4	101.8
38	B	1.0	91.7	92.6
39	B	0.3	93.8	94.1
Mean		3.0	93.1	96.2

Samples are ranked on the basis of antimony content.
[a] B = bracelet; E = earring; H = hair pin; K = key chain; N = necklace; P = pin.

may account for a significant fraction of the highly leaded jewelry items currently sold in the United States. In our original study (Weidenhamer and Clement, 2007a), almost one quarter of the 163 jewelry components tested contained 90% lead or more by weight.

While the evidence presented here for the recycling of battery lead is circumstantial, these results support the novel hypothesis that some battery lead is being recycled into highly leaded jewelry items. Other evidence (Weidenhamer and Clement, 2007b) suggests that leaded electronic solders are also being used to manufacture jewelry samples. If these leaded waste materials are being used in the manufacture of new consumer products such as children's jewelry, it suggests that policies designed to protect children's health by capping the lead content of jewelry and other products must also address the responsible recycling of leaded wastes.

4. Uncited reference

Q1 (US CPSC, 2005).

Acknowledgements

The National Science Foundation (DUE 9952552) provided financial support for the acquisition of the Varian 220 AA spectrometer used in these analyses.

References

Ahmed, F., 1996. The battery recycling loop: a European perspective. J. Power Sources 59, 107–111.

Associated Press, 2006. Reebok bracelets recalled for lead danger. <http://www.msnbc.msn.com/id/11974094/> (accessed 03.04.07).

CDC (Centers for Disease Control), 2006. Death of a child after ingestion of a metallic charm – Minnesota, 2006 Morbidity and Mortality Weekly Report 55, pp. 1–2.

Maas, R.P., Patch, S.C., Pandolfo, T.J., Druhan, J.L., Gandy, N.F., 2005. Lead content and exposure from children's and adult's jewelry products. Bull. Environ. Contam. Toxicol. 74, 437–444.

Prengaman, R.D., 2006. New low-antimony alloy for straps and cycling service in lead-acid batteries. J. Power Sources 158, 1110–1116.

US CPSC (US Consumer Product Safety Commission), 2005. Interim enforcement policy for children's metal jewelry containing lead – 2/3/2005. <http://www.cpsc.gov/BUSINFO/pbjewelgd.pdf> (accessed 03.04.07).

US CPSC, 2007. Advanced notice of proposed rulemaking. Federal Register 72, 921–923.

Weidenhamer, J.D., Clement, M.L., 2007a. Widespread lead contamination of imported low-cost jewelry in the US. Chemosphere 67, 961–965.

Weidenhamer, J.D., Clement, M.L., 2007b. Leaded electronic waste is a possible source material for lead-contaminated jewelry. Chemosphere. doi:10.1016/j.chemosphere.2007.04.023.

Please cite this article in press as: Weidenhamer, J.D., Clement, M.L., Evidence of recycling of lead battery waste into highly leaded jewelry, Chemosphere (2007), doi:10.1016/j.chemosphere.2007.06.005