The Nucleus ***53***, *No. 1 (2016) 9-13*

www.thenucleuspak.org.pk

The Nucleus

ISSN 0029-5698 (Print)

ISSN 2306-6539 (Online)

Presence of Toxic Metals and Their Effects in Finished Leather Goods

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ARTICLE INFO

Article history :

Received : 04 December, 2015

Revised : 26 January, 2016

Accepted : 03 February, 2016

Keywords :

Leather,
Heavy metals,
Atomic absorption spectroscopy

ABSTRACT

This study examines the presence of heavy metals in different types of leather finished goods. Various leather items like gloves, shoe soles and leather pieces for jackets were tested using Atomic Absorption Spectrophotometry and their toxic effects in our environment are discussed. Cadmium, lead and chromium are the most common heavy metals present in leather finished goods and are a cause for concern. Many countries in Europe and America have banned or limited their use in leather processing. This study reveals that the levels of heavy metals in most of the leather goods manufactured by different companies in Pakistan are within permissible limits. However, in some of the samples tested in this study, the amounts of cadmium, lead and chromium are considerably high which requires special attention from all stakeholders to bring it down to acceptable level. Failing to do so will be detrimental for export of these leather goods to Europe and America

1. Introduction

Every year Pakistan exports millions of dollars worth of leather based finished goods to Europe and America. In order to meet the requirements of World Trade Organization (WTO), Pakistani industry has to develop quality consciousness by upgrading its products to be competitive in the world markets. In Pakistan the leather industry including leather products is the third largest export sector after textiles and rice [1].

Along with textile garments the export of leather based finished goods brings large income/ foreign exchange to Pakistan. The export of leather finished goods has been steadily increasing since 2010 as shown in Fig. [1].

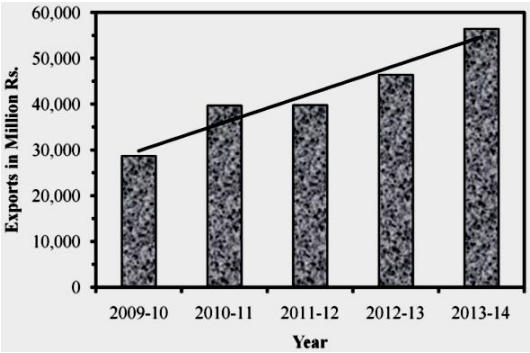

Fig. 1: Pakistani exports of leather and leather based goods (2009-14)

Due to low labour cost and changes in consumer demand, market for leather and footwear products is fast growing in developing countries. At the same time this market encounters the strictest requirements related to environment protection and health [2]. These days all leading international businesses seeking to import footwear and leather products from developing nations are not only concerned about the prices but they also want assurance that the products they are importing meet environmental standard requirements.

Due to the toxic effects of heavy metals American and European countries have promulgated several laws banning exports containing high levels of toxic heavy metals like Lead, Cadmium and Chromium [2]. The residue limits of these elements imposed by some important countries on leather and artificial leather are getting rigorous. The limits set by the European Union are given in Table 1.

Table 1: Permissible limits for heavy metals in leather and artificial leather goods set by European Union

Heavy Metal	Permissible Limit	Legislation
Cadmium	75 ppm	European Union EU EN71: Part 3 [2]
Lead	90 ppm	
Chromium	60 ppm	

The countries most affected by these laws are those which focus on leather tanning, finishing, leather products

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and artificial leather goods such as Brazil, Argentina, China, India, Pakistan and Turkey [3].

Leather making consists of many processes. In order to make leather from goat, cow or buffalo skin hides they have to pass through various processes. Tanning and dying are the two major processes used in the processing of leather. Mostly chemicals containing heavy metals like chromium, cadmium and lead are used in these processes [4]. As a result, leather finished goods contain these toxic heavy metals. This makes leather processing an environmentally challenging process [5].

Tanning is one of the most important processes in which raw hides and skins are converted into leather [5]. Tanning is the key process that renders stability to the skin matrix against microbial degradation, heat, sweat etc. There are two types of tanning processes. The first one is called chrome tanning and the second one is called vegetable tanning. Chromium (III) has been used widely in tanning for the excellent properties that it renders to the leather along with simplicity of operation [5]. Currently chrome tanning process is being used to process 80-90% of the total world production of leather [6]. Although the leather industry uses trivalent chromium based salts in the tanning process, the hexavalent chromium is present in the end products [7]. Hexavalent chromium is toxic in nature [8]. Due to the presence of chromium in finished leather and leather goods and its ability to leach from it, chromium sulfate tanned leather wastes are considered hazardous wastes [9]. Research work on removal of toxic metals from leather products has been done in some industries [10-13].

The other major process responsible for the presence of toxic metals like lead and cadmium in leather based products is dying of leather. Lead and cadmium based pigments are inexpensive and they form bright colours which is why they are used to colour leather and plastics [14, 15]. Lead and cadmium compounds are both toxic in nature. In this study we have analyzed different samples of finished leather goods for the presence of heavy metals like cadmium lead and chromium.

2. Experimental

Ten leather samples taken from gloves, jackets and shoe soles, as given in Table 2, were cut into tiny pieces. A sample of 3-4 grams was taken in a china crucible and was burned at 600 ^{o}C in a muffle furnace for 1 hr. When the sample was completely converted into ash, 5-10 ml of concentrated HNO_3 was added to it and then it was boiled for a few minutes. Then it was filtered in a 50 ml measuring flask. The volume of the flask was made upto the mark with double distilled water which was used as blank as well as for preparing both standard and sample solutions of required concentrations. Blank solution was first run 3 to 5 times before running the standard and sample solutions. Five different standard solutions (0.1, 0.5, 1.0, 2.5 and 5.0 ppm) for Pb, four different standard solutions (0.1, 0.5, 1.0, 2.5 and 5.0 ppm) for Cd and five different standard solutions (0.5, 1.0, 2.5, 5.0 and 10.0 ppm) for Cr were prepared. Correlation coefficients for Pb, Cd and Cr found in standard solutions were 0.9938, 0.9992 and 0.9937 respectively.

After sample solution preparation, the samples were analyzed with a Hitachi Z-8000 Atomic Absorption Spectrophotometer for the determination of cadmium, lead and chromium. For each of the ten samples, three individual sub-samples were measured in this study.

Table 2: Leather sample types used in this study

Sample Nos.	Sample Type
1-3	Glove
4-6	Jacket
7-10	Shoe Sole

3. Results and Discussion

3.1 Cadmium in Leather Goods

The permissible limit of cadmium in leather set by the European Union is 75 ppm as given in Table 1. Table 3 shows the results of cadmium present in the samples of leather. These results are plotted in Fig. 2 which shows that all the results are well within the range set by EU except for 2 samples which showed very high amount of cadmium present in leather. There is a large variation in the results for samples 4-6. This is because the measured concentrations are low in these samples. Cadmium present in Sample 1 and 8 is below detection limit (BDL) i.e., BDL<0.1 ppm. and hence not visible on the graph.

Table 3: Concentrations of Cadmium (ppm) in leather samples studied

Sample No.	Result 1	Result 2	Result 3	Mean	Standard deviation	% Standard deviation
1	BDL	BDL	BDL	BDL	BDL	BDL
2	2.1	2.0	2.1	2.1	0.1	2.8
3	24.3	22.9	23.0	23.4	0.8	3.3
4	1.3	1.6	1.8	1.6	0.3	16.1
5	0.6	0.5	0.8	0.6	0.2	24.1
6	0.2	0.3	0.9	0.5	0.4	81.1
7	2.3	2.8	2.6	2.6	0.3	9.8
8	BDL	BDL	BDL	BDL	BDL	BDL
9	161.7	162.0	162.8	162.2	0.6	0.4
10	453.4	457.0	460.7	457.0	3.7	0.8

BDL for Cd <0.1 ppm

Use of cadmium is restricted worldwide. Cadmium based pigments are extremely bright in colour. Cadmium yellow, cadmium red and cadmium orange are most commonly used cadmium pigments to colour leather and plastic. Chemically these consist of cadmium sulfide and

cadmium selenide. Cadmium compounds can cause testicular tumors, renal dysfunction, hypertension, arteriosclerosis, growth inhibition, cancer and chronic old age diseases. In addition cadmium may result in hemorrhagic lesions in sensory ganglia in the central nervous system [16].

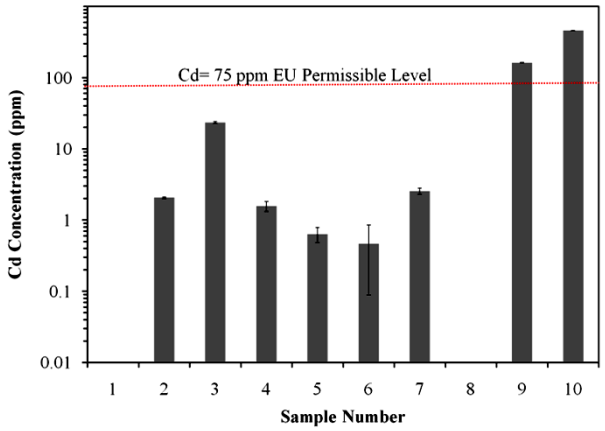

Fig. 2: Graph showing concentrations of cadmium in leather samples studied.

The use of cadmium containing pigments should be avoided in leather industry. The leather industry must be diligent in ensuring that cadmium based chemicals are kept to a minimum. Due to the toxicity of cadmium, these days it is replaced by Azo-pigments. Our study shows that still some of the manufacturers are using cadmium based pigments.

3.2 Lead in Leather Goods

Table shows the results of lead in leather. These results are plotted in Fig. .

Table 4: Concentrations of Lead (ppm) in leather samples studied

Sample No.	Result 1	Result 2	Result 3	Mean	Standard deviation	% Standard deviation
1	11.4	11.6	11.9	11.6	0.3	2.2
2	2.2	3.8	3.6	3.2	0.9	27.2
3	41.0	41.2	41.3	41.2	0.2	0.4
4	66.3	65.5	65.0	65.6	0.7	1.0
5	2072.5	2080.2	2095.4	2082.7	11.7	0.6
6	46.9	48.7	45.7	47.1	1.5	3.2
7	238.4	218.8	233.2	230.1	10.2	4.4
8	175.6	164.9	163.3	167.9	6.7	4.0
9	464.0	466.0	470.5	466.8	3.3	0.7
10	52.3	52.5	50.8	51.9	0.9	1.8

According to EU directive EN71/EEC the maximum permissible limit of lead to be present in leather is 90 ppm. Any product having lead above this threshold limit would be rejected by the EU. Most of the samples fall within the range set by the EU. However samples 5, 7, 8 and 9 contain high amount of lead in leather. The large variation in the results for sample 2 is because the measured concentration is low in this sample. The source of lead in leather is the colour pigments used in leather industry. Use of lead containing pigments should be avoided in leather industry.

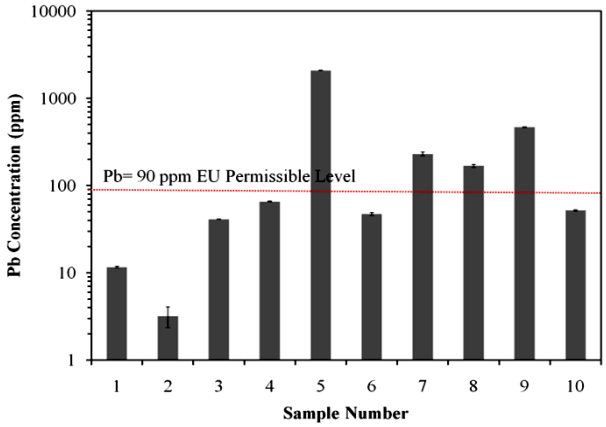

Fig. 3: Graph showing concentrations of lead in leather samples studied

Lead is a toxic metal and it is specially damaging to children under the age of 6 whose bodies are still developing. Lead causes nervous system damage, stunted growth and delayed development. It can cause kidney damage and affects every organ system of the body. It is also dangerous to adults, and can cause reproductive problems, both for men and women [17].

3.3 Chromium in Leather Goods

Table 5 shows the amounts of chromium present in leather samples investigated in this study. Results are plotted in Fig. 4.

Table 5: Concentrations of chromium (ppm) in leather samples studied

Sample No.	Result 1	Result 2	Result 3	Mean	Standard deviation	% Standard deviation
1	2661.4	2770.9	2728.6	2720	55.2	2.0
2	5.8	4.6	6.2	5.5	0.8	15.1
3	215.9	220.6	214.7	217	3.1	1.4
4	4.2	3.5	4.0	3.9	0.4	9.3
5	68.0	71.7	72.9	70.9	2.6	3.6
6	6.6	7.0	6.9	6.8	0.2	3.1
7	5758.7	5827.2	5838.7	5808	43.3	0.7
8	938.7	966.2	988.1	964	24.8	2.6
9	30.0	31.0	32.0	31.0	1.0	3.2
10	71.9	76.0	73.2	73.7	2.1	2.8

The permissible limit for chromium set by the EU is 60 ppm. From Table 5 and Fig 4 it can be seen that only 40% of the samples tested do fall within permissible limit. Large variation in results for sample 2 is because the measured concentration is low in this sample.

It is estimated that about 90% of all global tanned leather is tanned using chromium sulfate. While the rest are tanned using sulfates of other metals, usually aluminum or vegetable tannins or by using a combination of both. For leather tanning, use of chromium sulfate should be kept to a minimum.

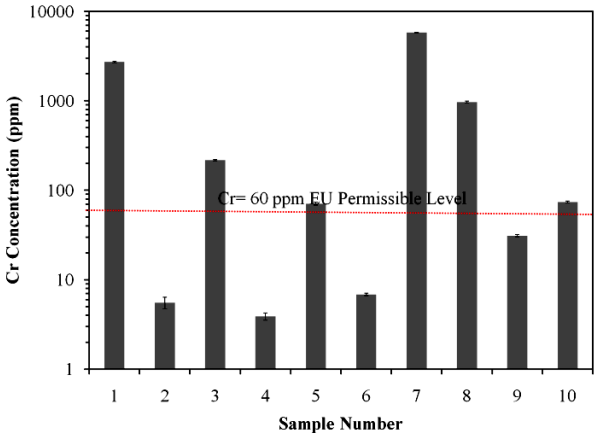

Fig. 4: Graph showing concentrations of chromium in leather samples studied

Table 6: Summary of results

Sample #	Sample type	Cd	Pb	Cr
1	Glove	Safe	Safe	Unsafe
2	Glove	Safe	Safe	Safe
3	Glove	Safe	Safe	Unsafe
4	Jacket	Safe	Safe	Safe
5	Jacket	Safe	Unsafe	Unsafe
6	Jacket	Safe	Safe	Safe
7	Shoe Sole	Safe	Unsafe	Unsafe
8	Shoe Sole	Safe	Unsafe	Unsafe
9	Shoe Sole	Unsafe	Unsafe	Safe
10	Shoe Sole	Unsafe	Safe	Unsafe
	Safe	80%	60%	40%
	Unsafe	20%	40%	60%

Skin exposure of the general public to chromium can occur from contact with products containing chromium, e.g., leather or preserved wood or chromium containing soil. After contact, inhalation or ingestion, the major toxic effects of hexavalent chromium can cause dermatitis/ allergic and eczematous skin reactions, skin and mucus membrane ulcerations, perforations of the nasal septum, allergic asthmatic reactions, bronchial carcinomas, gastro-enteritis, hepatocellular deficiency and renal oligoanuric deficiency [8].

Human studies have clearly established that inhaled chromium (VI) is a human carcinogen, resulting in an increased risk of lung cancer. Animal studies have shown chromium (VI) to cause lung tumor via inhalation exposure [18]. With such serious health risks, the amount of chromium present in samples of leather and leather based goods is matter of serious concern.

3.4 Health Effects

Gloves come into direct contact with our skin whereas shoe soles and jackets do not. Therefore any article comes into direct contact with the skin should be subjected to more stringent measures.

The present study of finished leather goods showed that 80% of the samples tested for concentration of cadmium were within the permissible limit set by EU. All samples taken from gloves and jackets showed that these products were safe. However, concentration of cadmium exceeded EU permissible limit in two out of four samples taken from shoe soles.

The study also revealed that when tested for concentration of lead, 60% of these samples were found within the permissible limit set by EU. All samples taken from gloves showed that these products were safe. However, concentration of lead exceeded EU permissible limit in one out of three samples taken from jackets and three out of four samples taken from shoe soles. This should be a source of concern for the manufacturers.

When the 10 leather samples were tested for concentration of chromium, it was found that only 40% were found within EU permissible limit. Concentration of chromium exceeded EU permissible limit in two out of three samples taken from gloves, one out of three samples taken from jackets and three out of four samples taken from shoe soles. All samples types (glove, jacket and shoe sole) exceeded EU permissible limit for chromium concentration in finished leather goods in this study. This is a serious problem and manufacturers need to take remedial measures or adopt alternate procedures to solve it.

Among the three sample types tested here for concentration of heavy toxic metals, gloves were found to be the best and shoe soles the worst. None of the samples taken from gloves exceeded EU permissible limits of Cd and Pb whereas samples taken from shoe soles showed that the concentration of at least two heavy metals was more than the EU permissible limit.

4. Conclusion

Presence of toxic metals like lead, chromium and cadmium in Pakistani finished leather goods is a cause of concern. Their amounts must be kept to minimum if not avoided completely. Cadmium and lead based pigments should not be used to dye leather. Instead azo based pigments should be used. Chromium sulfate used in the leather tanning process should be avoided. After chrome tanning excess of chromium should be washed or

removed from leather, so that the lowest quantity of chromium remains on leather.

Concerned authorities must ensure that the products of leather industry do not contain heavy metals exceeding permissible limits. Moreover there is a need to develop/identify and recommend ways of removing excess quantity of toxic elements from the finished products without damaging or diminishing their quality. This will minimize the risk to users of these products, and increase the number of leather products matching strict international safety and health standards which will qualify for exports and earn foreign exchange for the country.

Most importantly, it is in the greater interest of industrialists to ensure that the presence of heavy metals in their finished products does not exceed the permissible limits. Presence of toxic metals beyond acceptable limits will result in greater rejection rates. Consequently, the unit production cost but will increase and this will also bring bad repute for their industries, jeopardizing their export options.

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