(REFEREED RESEARCH)

DETERMINING THE HEAVY METAL CONTENTS OF NATURAL AND ARTIFICIAL UPHOLSTERY LEATHERS

DÖŞEMELİK DOĞAL VE YAPAY DERİLERİN AĞIR METAL İÇERİKLERİNİN BELİRLENMESİ

Ahmet ASLAN[1*], Nuray Olcay (IŞIK) ÜZÜM[2]

[1]Ege University, Department of Leather Engineering, İzmir, Turkey
[2]Namık Kemal University, Department of Leather Technology, Tekirdağ, Turkey

Received: 11.02.2014 Accepted: 30.01.2015

ABSTRACT

In this study, the amounts in natural and artificial leathers of heavy metals such as cadmium, cobalt, chrome, copper, mercury, nickel and lead, which are limited in many goods due to their toxicological features, and of aluminum and zinc, which are unlimited, were determined. First, the wet decomposition and the total heavy metal contents of the leathers were specified in ICP-OES. Later, the amount of heavy metal manifesting when the leathers were exposed to sweat and water was determined using ICP-OES. The heavy metal detected in the greatest quantities in natural and artificial leathers was chrome. Small amounts of aluminum, cobalt, copper, nickel and zinc were also determined due to the chemical and physical reactions during the dyeing and finishing processes,. However, neither hexavalent chrome, cadmium, mercury nor lead were encountered in either of the leather types. Finally, heavy metal contents were compared with standard limit values.

Keywords: Natural upholstery leather, artificial upholstery leather, heavy metal, ICP-OES, environment.

ÖZET

Bu çalışmada toksikolojik özelliklerinden dolayı birçok kullanım eşyasında bulunmasına sınırlamalar getirilen kadmiyum, kobalt, krom, bakır, civa, nikel, kurşun ve sınırlandırma getirilmeyen alüminyum ve çinko gibi ağır metallerin döşemelik doğal ve yapay derilerdeki miktarları tespit edilmiştir. Araştırmada; öncelikle derilerin yaş yakma işlemi ile toplam ağır metal içerikleri ICP-OES de belirlenmiştir. Daha sonra, derilerin kullanımı esnasında tere ve suya maruz kalmasıyla açığa çıkan ağır metal miktarları ICP-OES kullanılarak saptanmıştır. Doğal ve yapay derilerde saptanan en yüksek ağır metal elementinin krom olduğu tespit edilmiştir. Boyama ve finisaj prosesleri esnasındaki kimyasal ve fiziksel reaksiyonlardan dolayı küçük miktarlarda alüminyum, kobalt, bakır, nikel ve çinko elementleri tespit edilmiştir. Ayrıca her iki deri tipinde de hekzavalent krom, kadmiyum, civa ve kurşun metallerine rastlanılamamıştır. Son olarak da, ağır metal içerikleri, standart limit değerler ile kıyaslanmıştır.

Anahtar kelimeler: Döşemelik doğal deri, döşemelik yapay deri, ağır metal, ICP-OES, çevre.

Corresponding Author: Ahmet Aslan, ahmetaslan@gmail.com, Tel. +90 232 311 26 44 Fax: +90 232 342 53 76

1. INTRODUCTION

Today, natural leather production is regarded as an industry which causes significant pollution. Many different organic and inorganic materials are used during the manufacture of leather, and pollution is caused by the intense use and discharge these chemicals (1). The manufacture of nearly 90% of the natural leathers produced in the world still involves the use of chrome salts (2). However, chrome cannot give the leather all the features and qualities desired, and so different metal salts, vegetable tannins and/or synthetic tannins are used in various phases of leather manufacture. In addition, dyes and pigments containing heavy metals are used to color the natural leather. Some of the heavy metals in the natural leathers may originate from the metal based chemicals used in the many steps of leather manufacture, heavy metals in the water used in processing, or contamination from mechanical processes (3). Finally, they may have been transferred to the leather through the metabolic activities of the animal while it was alive. In artificial leathers, heavy metal content is generally the result of the contents of the chemicals and pigments and contamination during manufacturing, since these leathers

are not subjected to a lengthy tanning process in which heavy metals are used in large quantities.

Recently, the increasing price of natural leather around the world has caused consumers to shift towards goods manufactured from artificial leathers. Since these products are easy to clean, light, and have good water-repelling features, they are used as an alternative to natural leather especially in shoes and furniture. However, artificial leathers cannot replace natural leathers in terms of comfort and hygiene, especially in shoes, so that the demands of discerning consumers for organic products are increasing, and the demand for natural leather has not decreased (4).

All leather products whose lifetime has ended can be harmful to the ecosystem when discarded into the environment (5). This, combined with increasing environmental awareness and the demands of consumers for organic and hygienic products, has caused an increase in toxicological research into leather (6).

As a result of the ecological and toxicological dangers of the leather industry, bans or limitations have been imposed on the use of toxicological chemicals (7), and there has been a move towards cleaner manufacturing systems and technologies. The effects on human health of these chemicals, in addition to their effects on environmental pollution, are being investigated because of their use in leather products (3).

In the manifesto of the European Union Commission dated July 12 2002, a complete ban was placed on Pb, Cd, Cr (VI), As, Hg and their compounds in textile and leather products, and concentrations of other heavy metals were limited (8). After this manifesto, it was necessary for leather industries to manufacture with more awareness and supervision. Studies were carried out to determine the heavy metal content both of various textile materials and of natural leathers (3, 5, 7). However, no comparisons have been conducted between the heavy metal content of these two types of material, which can be used as alternatives in the manufacture of finished goods. Therefore, the aim of this research was to determine the heavy metal contents of natural and artificial leathers used in furniture. The total heavy metal ions in leathers and the heavy metal ions that can be extracted in artificial sweat solution were determined using ICP-OES. Later, an evaluation was made of the difference between the total amounts of heavy metal in the natural and artificial leathers and their extraction levels in artificial sweat solution.

2. MATERIAL AND METHOD

2.1. Material

Ten natural and ten artificial different finished upholstery leathers of different colors were randomly selected as research material and obtained from the Istanbul Leather Industrial Area and Menemen/Izmir Leather Free Zone, and from leather furniture manufacturers.

2.2. Method

First, the pH contents of the leathers were determined in accordance with ISO 4045:2008 and their total sulfate ash was assessed in accordance with ISO 4047:1977 (9).

Leather samples supplied as research material were prepared in accordance with ISO 4044: 2008 and samples were taken in accordance with ISO 2418:2002 (9).

In order to determine the amounts of heavy metals in the leather products which could be extracted in damp conditions, extraction in water (EW) was carried out on the samples in accordance with ISO 4098:2005, and extractable heavy metal levels were determined with ICP-OES (Perkin Elmer Optima 2100 DV) (9).

In order to determine the amounts of heavy metal which can get into human sweat due to its dissolving effects when the leathers are in use, an artificial sweat solution was prepared in accordance with ISO 105-E04: 2014 (10). After the extraction process was performed on leather samples in the artificial sweat solution (EAS) in accordance with ISO 17072-1:2011, the concentration levels of heavy metals other than hexavalent chrome were determined by ICP-OES (3). The total amount of heavy metals (THM) other than hexavalent chrome within the samples was determined by ICP-OES in accordance with ISO 17072-1:2011 (9). The amount of hexavalent chrome in the samples was determined in accordance with ISO 1705:2007 (9).

MS Excel software was used for statistical evaluation of the data obtained.

3. RESULTS AND DISCUSSION

The physical features of leathers may vary based on the manufacturing methods and the structure of the chemicals used during manufacturing (11). The pH and ash values of the leathers in the study are displayed in Table 1.

The pH values of leathers may vary in accordance with the pH values of the chemicals and additives used in the final steps of the leather manufacturing process and the proportions in which they are used. The pH values for liquid extracts at a ratio of 1:20 should not be below 3.5 (12). As seen in Table 1, it was found that the average pH value of the natural leathers in our study was 4.88±0.23 and that of the artificial leathers was 7.32± 0.59. These pH values match the standard value of BASF (2010) (12).

The total amount of inorganic material in leathers can be found by the ash determination method, and should not exceed 2.5% (12). Also, 0.5% mineral material may be found in natural leathers based on the nutrition condition of the animal (12). Cantera et al. (1994) and Taylor et al. (1997) found 6.7% and 8.5% total ash values respectively in accordance with the tanning method with chrome (13, 14). Rajamaran et al. (1978) found the amount of ash in vegetable and vegetable-chrome tanned natural leathers to be 7.42% and 6.45% (15). Tatano et al. (2012) found an average amount of ash in the synthetic leathers of 16.61% (16).

When the ash values in our research were examined, it was found that the average amount of ash was 7.38±2.89% for natural leathers and 2.95±1.89% for artificial leathers (Table 1). It was found that all the ash values in our research were higher than the standard value. Values found in natural leathers were similar to those found in works by other researchers, while artificial leathers had lower values.

Table 1. pH and ash amounts of the leathers

Parameters	Natural Leathers	Artificial Leathers	Standard
	Mean ± SD	Mean ± SD	BASF[1]
pH	4.88 ± 0.23	7.32 ± 0.59	>3.5
Ash (%)	7.38 ± 2.89	2.95 ± 1.89	<2.5

[1] Pocket Book for the Leather Technologist

Today, the fact that consumer demand is shifting towards organic and non-toxic materials necessitates deeper examination of heavy metals, especially in leather products in contact with human skin.

It was found in this study that the values of all heavy metals in the leathers determined by wet decomposition were higher than those which could be extracted in water or sweat (17, 18). As indicated in Table 2, cadmium, mercury and lead were not found among the heavy metal ions. Basaran et al. (2006) found cadmium and lead at very low levels (3). They stated that the amounts of cadmium determined at low levels varied according to the color of leathers, and that this resulted from pigments used in the leather production process (3). Besides, the very low levels of lead and mercury which can sometimes be determined in natural leather samples may derive from the environment of the animal or the slaughterhouse.

EW and EAS cobalt concentration values of natural leathers have been observed below the standard values and THM cobalt concentration values have been observed which were above the standards (17, 18). Cobalt may have originated from bioaccumulation while animal was alive; from the colorants used for dyeing the leathers, or from the machines used during the processing of the leathers (3, 5, 19, 20). Also, it has been found that total cobalt concentration values of artificial leathers were below the limits reported in Eko-Text 100 and SG standard values (17, 18). This low cobalt content of artificial leathers may be a result of metal complex pigments and contamination during production (20, 21).

In our study, the heavy metal with the highest extract among the natural manufactured leathers was found to be chrome (Table 2). This high amount of chrome is the result of the fact that tanning is mostly done with chrome sulfate salts in today's technology. Manufactured goods tanned with chrome contain at least 2.5% Cr_2O_3 (12). Calculated by the atomic weights of chrome and oxygen, this amounts to approximately 17100 ppm chrome. When the EW, EAS and THM contents of the artificial leathers were compared with the Eco-Text and SG standards provided in Table 2, all the values except Cr complied with the standards (17, 18). This high chrome content may be a result of colorants and contamination during mechanical processes (20, 21).

Cr (VI) was not detected in EA, EAS and THM samples of natural and artificial leathers. Cr (VI) cannot be detected under 3 ppm when using ISO 17075:2007 in the determination of Cr (VI) (9). On 26 March 2014, the European Union prohibited amounts of Cr (VI in leather products of 3 ppm or more. This regulation will be effective from 1 May 2015 (22). As seen in Table 2, maximum Cr (VI) concentrations stipulated by SG and Eko Text 100 are much lower than the maximum limit value required by the EU (17, 18). Hexavalent chrome is never used in the production of natural leathers due to its carcinogenic effects. However trivalent chrome, which may be present in a free state and not bound to the leather, can be oxidized to the hexavalent chrome under suitable conditions, or the hexavalent chrome in leather products may result from contamination during production (23). Similarly, the hexavalent chrome that may be detected in artificial leathers can be caused by the contamination during production.

Table 2. Heavy metal content of leathers

Metals	Natural Leathers			Artificial Leather			Standards	
	EW[1] (ppm)	EAS[2] (ppm)	THM[3] (ppm)	EW[1] (ppm)	EAS[2] (ppm)	THM[3] (ppm)	Eko-Tex 100 (ppm)	SG[4] (ppm)
	Mean±SD	Mean±SD	Mean±SD	Mean±SD	Mean±SD	Mean±SD		
Cd	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.10	0.10
Pb	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	1.00	0.80
Hg	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.02	0.02
Co	0.85±0.46	2.94±2.86	31.74±29.86	0.07±0.03	0.08±0.01	0.55±0.37	4.00	4.00
Cr	72.57±31.12	168.42±38.24	16 549.00±207.25	2.09±2.01	11.48±4.69	96.90±46.48	2.00	-
Cr(VI)	N.D[5].	N.D.	N.D.	N.D.	N.D.	N.D.	0.50	0.30
Cu	4.11±3.47	6.57±11.10	53.74±40.60	0.00±0.00	0.03±0.01	0.35±0.88	50.00	60.00
Ni	0.00±0.00	0.11±0.25	0.89±2.72	0.00±0.00	0.00±0.00	0.01±0.01	4.00	1.00
Zn	0.13±0.10	1.23±0.86	11.93±10.45	0.00±0.00	0.01±0.02	0.001±0.00	-	-
Al	40.87±39.12	77.13±54.41	602.33±284.65	0.78±0.52	1.32±0.22	4.73±4.25	-	-

[1] level of heavy metals extractable in water
[2] levels of heavy metals extractable in artificial sweat solution
[3] total amount of heavy metal in samples
[4] SchadstoffGeprüft – The Test Mark for low-pollutant leather products
[5] Not detected

EW and EAS copper concentration values determined in natural leathers have been found to comply with limit values set by Eko-Tex 100 and SG, and the THM copper value of natural leathers has been determined to be above the 50ppm indicated by Eko Tex 100, and below the 60ppm required by SG (17, 18). The copper detected in natural leathers may be caused by contamination during the production of leathers and metal complex based dyes used in coloring leathers (3, 20). When Table 2 is examined, it can be seen that the entire copper concentration values of artificial leathers are much lower than the standard values (17, 18). while the copper concentrations detected in artificial leathers, may result from contamination during production and copper based dyes.

Nickel concentration values of EW, EAS and THM present in natural and artificial leathers have been found to be below the standards (17,18). Nickel values detected in both leather types might be caused by dyestuffs used in leather production or stainless steel based machines and tools (3, 19, 20).

Because of a lack of limit values for zinc and aluminum by both SG and Eko-Tex 100, it was not possible to evaluate conformity with standards for the Zn and Al values detected in our study (Table 2). The presence of these metals determined in both leather types may have been caused by contamination, inorganic pigments, or the water used in the production of the leathers (3, 19, 20). Besides Zn may have originated from the metabolic activities of the animal while it was alive, and aluminum is used during the tanning and retanning of the natural leathers (5).

4. CONCLUSION

In line with the increase in the awareness of the role of pollution in human health today, ecological and toxicological limitations and bans have been introduced. As a result of these topics gaining currency, determination of heavy metals as potentially harmful materials has become crucial. Accordingly, an analysis was made of the heavy metals which could be extracted from natural and synthetic upholstery leathers by solution in water and sweat, with the aim of determining their negative effects on humans and the environment.

Cadmium, lead, mercury and hexavalent chrome elements were not detected in natural leathers. While nickel was found at very low quantities in natural leathers, cobalt and copper were determined in large quantities. It was observed that the high chrome contents were due to the use of chrome in the tanning process. There have as yet been no clinical findings showing that the chrome present in leather harm human health, and it is very difficult to achieve the limit values set by Eko Text 100 and SG in natural leathers. Heavy metal contents found in finished natural leathers have been understood to be usually caused by chemical substances, dyes and pigments used in leather production processes. Besides, contamination during the production process of the leather, and the feeding conditions and the environment of animals when alive also affect the heavy metal contents of natural leathers.

The results for heavy metals in artificial leathers are similar to those for heavy metals in natural leathers. However, the heavy metal contents determined in artificial leathers are much lower than those in natural leathers. This is because mineral tannins are not used in the production of artificial leathers. Although cadmium, lead, mercury and hexavalent chrome were not found in artificial leathers, and nickel element was detected at very low levels, only chrome was found in high quantities. The occurrence of these heavy metals in artificial leathers may be caused by chemical substances, dyes and pigments used in production process and by contamination from various sources.

To conclude, it is expected that in the future the trend towards a demand for ecological products will have a greater effect on leather producers but that the suggested limit values may be decreased further. Therefore, the leather industry and especially natural leather processing should be prepared for these new lower limit values. Otherwise, the natural leather industry will be unable to keep up with worldwide competition, and may be affected adversely.

REFERENCES

1. Zhang, M., Zhang, M. 2006, " Assessing the Impact of Leather Industry to Water Quality in the Aojing Watershed in Zhejiang province, China", *Environmental Monitoring and Assessment*, Vol:115, pp:321-333.
2. Aslan, A. And Gülümser, G., 2011, "Evaluation of Chrome-Tanned Leather Solid Wastes as Lubricating Filler Agents", *Tekstil ve Konfeksiyon*, Vol:21, pp:405-409.
3. Basaran, B., Iscan, M., Bitlisli, B.O., et al., 2006, "Heavy Metal Contents of Various Finished Leathers", *Journal of the Society of Leather Technologists and Chemists*, Vol. 90(6), pp: 229-234.
4. Bitlisli, B.O., Karavana, H.A., Basaran, B. and Aslan, A., 2005, "Importance of Using Genuine Leather in Shoe Production in Terms of Foot Comfort", *Journal of the Society of Leather Technologists and Chemists* , Vol: 89, pp: 107-110.
5. Aslan, A., 2009, "Determination of Heavy Metal Toxicity of Finished Leather Solid Waste", *Bulletin Of Environmental Contaminatıon and Toxicology*, Vol:82 pp: 633-638.
6. BLC, 2010, "Reach Update", *Leather International*, Vol: September, pp:14-15.
7. Özdoğan, E., Korkmaz, A. Seventekin, N., 2007, "Eco-Tex and EU Eco Label", *Tekstil ve Konfeksiyon*, Vol: 17, pp:149-152.
8. European Commission, 2004. "Official Journal of the European Communities", http://europa.eu.int/comm/environment/ecolabel/pdf/furniture/draft_ criteria_furniture _june2002.pdf (20 Kasım 2004).
9. ISO, 2014, "The International Union of Leather Technologists and Chemists Societies", http://www.iso.org/iso/iso_catalogue/catalogue_ tc/catalogue_tc_browse. htm?commid=55240&development=on (03 Ocak 2014).
10. ISO, 2013, "ISO 105-E04:2013 Textiles -- Tests for Colour Fastness - Part E04: Colour Fastness to Perspiration", *International Organization for Standardization*, Switzerland.

11. Aslan, A., 2013, “Improving the Dyeing Properties of Vegetable Tanned Leathers Using Chitosan Formate”, *Ekoloji,* Vol: 22, pp:26-35.

12. BASF, 2010, “Pocket Book for the Leather Technologist”, http://visdombasfcrm.com/lp/Blue%20book.pdf (04 Nisan 2010).

13. Cantera, C.S., Greco, C.A. and Guisti, M., 1994, “Dechroming of Shavings.Part 1. Enzymic Alkaline Treatment. Study of Variables”, *Das Leder*, Vol: 11, pp:265-270.

14. Taylor M. M., Diendorf E. J. and Thompson C. J., 1997, “Extraction of Value Byproducts From the Treatment of Chromium Containing Collagenous Leather Industry Waste”, *Journal of the Society of Leather Technologists and Chemists*, Vol:81, pp:5-13.

15. Rajamaran, R., Poorneswari, S., Bangaruswamy, S., Rao, J.B. and Santappa, M., 1978, “Influence of Different Tanning Systems on the Characteristics of Leather”, *Leather Science*, Vol: 25, pp:394–399.

16. Tatano, Fabio; Acerbi, Nadia; Monterubbiano, Chiara; et al., 2012, “Shoe Manufacturing Wastes: Characterisation of Properties and Recovery Options”, R*esources Conservation and Recycling”*, Vol: 66, pp: 66-75.

17 SG, 2006, “The Test Mark for Low Pollutant Leather Products”, http://www.ecco.com/downloads/ECCO_SGlist.pdf (22 Kasım 2010).

18 Oeko-Tex Standard 100, 2010, “Limit Values and Fastness, Part 1”, http://www.oekotex.com/xdesk/ximages/470/16132_grenzwerte.pdf (22 Kasım 2010).

19. Harmancıoglu, M., Dikmelik, Y., 1993, “Inorganic Substances of Hide and Skin”, *Raw Skin*, Özen Press, Izmir, Turkey, pp: 207-210.

20. John G., 1997, “Finishing”, *Possible Defects In Leather Production*. Druck Partner Rübelman GmbH, Germany, pp: 158-209.

21. Graf, D., 2001, “Formation of Cr (VI) Traces in Chrome Tanned Leather: Causes, Prevention and Latest Findings”, *Journal of the American Leather Chemists Association*, 96, pp: 169-179.

22. Barroso J. M., 2014, “Regulations”, *Official Journal of the European Union,* 90, pp: 1-3.

23. Basaran, B., Isik, N.O., 2007, “Cr(VI) Formation in Double-Face Sheepskins: Effect of Chromium Level and Ironing Temperature”, *Journal of the Society of Leather Technologists and Chemists*, Vol. 91(1), pp: 4-10.