

Heavy Metal Contents Of Bootee Leathers Tanned With Different Process Recipes

Farklı İşlenti Reçeteleri ile Tabaklanmış Bebek Patiği Derilerinin Ağır Metal İçerikleri

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SUMMARY

The purpose of this work was to determine the content of heavy metals such as antimony, arsenic, barium, cadmium, chromium, lead, mercury, selenium in leather used by producing baby booties and to compare the limit values for leather and textiles. It was concluded that heavy metal content of finished leathers depended mainly on the chemicals used in processing; in particular, high chromium contents were determined. Moreover, small amounts of antimony, arsenic, barium, cadmium, lead, mercury and selenium deriving from chemical and physical reactions during dyeing and finishing processes were detected.

Keywords: Bootee Leather, Baby, Heavy Metal, Tanning, Finishing.

ÖZET

Bebek patiği üretiminde kullanılan derilerdeki selenyum, civa, kurşun, krom, kadmiyum, baryum, arsenik ve antimon gibi ağır metal içeriklerinin belirlenerek elde edilen sonuçların deri ve tekstillere ait limit değerler ile karşılaştırılması bu çalışmanın amacını oluşturmaktadır. Mamul derilerdeki ağır metal içeriğinin çoğunlukla işlente kullanılmış olan kimyasallara bağlı olduğu sonucuna varılmıştır. Özellikle, krom içeriğinin oldukça yüksek olduğu tespit edilmiştir. Diğer taraftan, boyama ve finisaj işlemleri sırasında meydana gelen kimyasal ve fiziksel reaksiyonlar sonucu ortaya çıkan selenyum, civa, kurşun, kadmiyum, baryum, arsenik ve antimon içeriğinin ise daha düşük miktarlarda olduğu belirlenmiştir.

Anahtar Kelimeler: Bebek patiği derisi, Bebek, Ağır metal, Tabaklama, Finisaj

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Introduction

Twentieth century was an era when ecological issues were raised by the environmentalists, and biological compatibility is discussed in academic platform more than ever. Thus, consumers have started to question the ecological and toxicological features of products as well as appearance, durability, colour and other physical characteristics. Like other industries, the leather industry is under considerable pressure from this to match the “clean production” principles and innovations in production technology. In the same way, toxic chemicals have been banned in all kind of goods ¹.

Since children are very sensitive to toxic substances, there is major concern for babies. Thus; the issue of the hazard of children's goods must be considered. However; in spite of the hazards due to sucking, licking or swallowing, bearing in mind the normal and foreseeable behaviour of children, children's product are not covered by the standard BS EN 71-3:1995, BS 5665-3:1995 ². Some heavy metals have important beneficial effects on metabolic activities as trace metals, but they can be toxic in high concentration in the body. The health risks of heavy metals are due to their bioaccumulation capability; heavy metals accumulate because they are not metabolized in the body, and may accordingly build up to harmful levels ³. The European standard on safety of toys on banning the existence of Sb, As, Ba, Cd, Cr, Pb, Hg and Se, shows that this issue has become very sensitive and will be on the agenda of the leather industry from now on ⁴.

In view of the importance of the issue in the EU, this study aimed to determine and compare the heavy metal contents of babies' bootee leathers made according to various production recipes. The amounts of heavy metal ions of finished leathers in acid solutions were determined according to EN 71 by ICP-OES, and assessed.

Material and Methods

In this study, 12 pieces of finished bootee leathers which were obtained for the use in children's products by processing sheepskins were examined. The skins were processed, in three different groups of 4 pieces each, according to recipes shown in *Table 1* and they were all treated same finishing process recipe as shown in *Table 2*.

Test pieces from finished bootee leathers were cut and ground according to IUC 3 ⁵. A precisely weighed 2.0 g leather sample was placed in a flask with 100 ml of HCl

solution (0.07 mol/l). Then, the solution was adjusted pH 1-1.5 using HCl solution (2 mol/l). The container was placed on a shaker (50 rpm) for 1 h. Then, this solution left in dark place for 1 h. After that, filtration was performed using a membrane filter with pore size 0.45 µm and the liquid phase containing heavy metals were detected by using ICP-OES according to BS EN 71-3:1995, BS 5665-3:1995 ². Outputs were analysed by using SPSS 15.0 statistical package. The GLM method was used to compare mean values among treatments and the Duncan test was used to identify significant differences ($p < 0.05$) among the groups.

Results and Discussions

Heavy metals, known as transition metals, occupy a considerable part in the periodic table, and are of high atomic mass; they can be a high ecological risk when they accumulate in soil and organisms ⁶. The effects of their accumulation must be taken into account when considering the increased expectation of life quality. In addition, their restrictions in consumer products have had a significant impact on industrial developments.

Leather manufacturing is in a state of constant technological development. Society has started to demand a reduction in heavy metals used in leather processing. Although it has not been possible so far to eliminate their use completely, there has been a decrease in the use of heavy metals in tanning and some advance toward metal-free tanning methods. However; the advantages of metals in tanning are such that it is reported that 90% of today's leather products are tanned with chromium salts ⁷. Al and Zr are used in tanning and retanning as a substitute for chromium salts, and various metal salts are also used in other processes. It is generally believed that heavy metal content in finished leathers is caused not only by tanning processes but also by metabolic activities during the animal's life, utilization of chemicals based on metal salts at different stages of manufacturing and the heavy metal content of the water used in processing, or by physical contamination from the machinery used in processing.

Today, with the increasing of ecological focus on avoiding any substance that is toxic to humans or the environment, it has become more important to investigate thoroughly the effect of garments and shoes when they come into contact with the skin. The food chain is not only way in which hazardous substances are taken into the body; toxic heavy metals may also be taken up from clothes and other products.

Therefore, the possibility of leachable heavy metal contents of garments as well as shoes causing toxic effects in humans must be considered.

Children are particularly susceptible to metal exposure due to their tendency to explore objects by physical contact.

Also, a baby's body is more liable to take in these metal ions by any casual skin contact, and therefore leachable heavy metals have much greater importance as a health hazard for babies. It was the aim of this study to evaluate heavy metal uptake from leather booties and to assess the accumulation risks in a baby's body.

Table 1. Tanning process recipes.

Process	Chemical Additives	Chrome Tanning	Semi Chrome Tanning	Chrome Free Tanning	Process Remarks
Pickle	Water (25 °C)	80 %	100 %	100 %	
	Salt	7 Bé°	7 Bé°	9 Bé°	
	Dicarboxylic Acid	-	1 %	1.5 %	
	Acid	2.2 %	2 %	2.5 %	pH: 3.2
	Polyaldehyde	1 %	2 %	2.5 %	
	Synthetic Esters	1.5 %	1.5 %	2 %	
Tanning	Basic Chromium Sulphate (26 %)	8 %	4 %	-	
	Blends of Phenolic Retanning Auxiliaries	-	4 %	4 %	
	Zirconium Sulphate (30 %)	-	-	10 %	
	Basic Aluminium Complex Salt (17 %)	-	-	2 %	
	Blends of Organic Acid Salts	1 %	1 %	1 %	
	Sodium Formate	1.5 %	1 %	0.8 %	
	Sodium Bicarbonate	1.5 %	1.2 %	1.2 %	pH: 4.2, Drain
Pre-Retenage and Neutralisation	Water (35 °C)	180 %	180 %	150 %	
	Aliphatic Dicarboxylic Acid for High Exhaustion	1 %	0.8 %	0.8 %	
	Basic Chromium Sulphate	2 %	2.5 %	-	
	Neutralised Naphthalene Sulfonic Acids	1.5 %	2 %	2 %	
	Phosphated Fatty Alcohols and Synthetic Esters	2 %	2 %	2.5 %	
	Sodium Formate	2 %	1.5 %	1.5 %	
	Sodium Acetate	-	0.8 %	1.5 %	
	Sodium Bicarbonate	0.6 %	0.6 %	1 %	pH: 5.5
Retenage and Fatliquoring	Replacement Syntan	3 %	3 %	4 %	
	Auxiliary Syntan For Penetration	2 %	2 %	2 %	
	Modified Amino Resin	3 %	3 %	4 %	
	Blend of Vegetable Extracts	6 %	6 %	8 %	
	Acrylic Copolymer Emulsion	3 %	3 %	3 %	
	Sulphated Blends of Synthetic Spem oils, Neatsfoot and Vegetable Oils	4 %	2 %	4 %	
	High Molecular Ester Sulphonates (Sulphonated Carboxylic Acid Esters / Complex Active Emulsifier)	2 %	5 %	5 %	
	Polimeric Softening Agent	2 %	1 %	1 %	
	Acid Dyestuffs	4 %	4 %	4 %	
	Formic Acid	4 %	4 %	4 %	pH: 3.8, Drain

Table 2. Finishing process recipes

Chemical Used	Spray I	Spray II	Spray III
Water	420	500	100
Pigment Paste	100	150	-
Acrylate Copolymer Dispersion	140	120	-
Polyurethan Emulsion	60	80	-
Acrylic Micronbinder	80	80	-
Casein Emulsion	40	60	-
Wax Emulsion	20	25	10
Nitrocellulose Emulsion	-	-	100
Hand Modifier	-	-	15
Coating Dosage (g/sqft)	2xSpray (6 and 4)	7	7

In the study, a comparison was made of leathers produced in the conventional way and those produced using modified recipes by dissolving their various heavy metals in acidic solutions, in order to assess the risk of build-up of these metals in children's bodies. The modified recipes were composed the same basis as shown in *Table 1* and all leathers were treated same finishing process recipe as

shown in *Table 2*. The accumulation risks of heavy metals from leather products after modified leather processes were determined as shown in *Table 3* ^{2, 8, 9, 10}.

The heavy metal contents of baby bootee leathers determined by leaching with acid solution according to BS EN 71-3 (1995) are given in *Table 3*. The concentrations of

Table 3. Heavy metal contents of leathers (ppm)

Heavy Metals	n		Chromium Leather	Semi-Chromium Leather	Chromium-Free Leather	Limit Values in BS EN 71-3
Antimony (Sb)	4	Min.	1.25	1.63	1.26	60
	4	Max.	1.75	2.01	1.57	
	4	Mean±S.E.M	1.45±0.11 ^b	1.85±0.08 ^a	1.41±0.06 ^b	
Arsenic (As)	4	Min.	0.55	0.68	0.69	25
	4	Max.	0.75	0.78	0.81	
	4	Mean±S.E.M	0.63±0.04 ^b	0.73±0.02 ^a	0.74±0.03 ^a	
Barium (Ba)	4	Min.	0.83	1.02	1.53	1000
	4	Max.	1.01	1.90	1.91	
	4	Mean±S.E.M	0.91±0.04 ^b	1.58±0.20 ^b	1.76±0.08 ^a	
Cadmium (Cd)	4	Min.	0.98	1.74	1.54	75
	4	Max.	1.82	1.97	1.95	
	4	Mean±S.E.M	1.28±0.19 ^b	1.88±0.05 ^a	1.76±0.08 ^a	
Chromium (Cr)	4	Min.	28545.00	13750.00	0.21	60
	4	Max.	30823.00	15023.00	0.25	
	4	Mean±S.E.M	29613.75±477.06 ^a	14405.25±323.68 ^b	0.23±0.01 ^c	
Lead (Pb)	4	Min.	1.15	1.28	1.37	90
	4	Max.	1.32	1.63	1.55	
	4	Mean±S.E.M	1.21±0.04 ^b	1.51±0.08 ^a	1.45±0.04 ^a	
Mercury (Hg)	4	Min.	0.45	0.46	0.45	60
	4	Max.	0.54	0.49	0.62	
	4	Mean±S.E.M	0.51±0.02 ^a	0.48±0.01 ^a	0.52±0.04 ^a	
Selenium (Se)	4	Min.	1.52	1.48	1.48	500
	4	Max.	1.81	1.68	1.65	
	4	Mean±S.E.M	1.63±0.07 ^a	1.56±0.05 ^a	1.58±0.04 ^a	

^{a, b, c;} different letters

in the same line indicate significant differences among the groups (p<0.05).

antimony leachable in acid solutions of all leathers were determined to be lower than the BS EN 71-3 (1995) test limit of 60 mg/kg. The presence antimony may be due to the metal salts in the dyes and fixing agents for dyes used in leather production ^{11, 14}.

Amounts of arsenic leachable in acid solutions were found to be below the limit value for bootee leathers of 25 ppm suggested in BS EN 71-3 (1995). However, amounts of leachable arsenic for all bootee leathers were found to be higher than the limit value of 0.2 mg/kg in the SG list ¹⁵. Arsenic concentrations detected in the leathers are attributable to pesticides and water used in leather processing ^{16, 17}.

In barium analysis, leachable barium contents of the leathers were found to be lower than the BS EN 71-3 (1995) test limit of 1000 mg/kg. The barium may have been due to the metal salts within pigments used in leather production ^{11, 12, 18}.

The amount of cadmium leachable in acid solution was lower than limit values of 75 mg/kg ². However, amounts of leachable cadmium for all leathers were found to be higher than the limit value of 0.1 mg/kg in the SG list ¹⁵. High cadmium concentrations were detected, because cadmium compounds are the metal salts which forms certain pigment colours used in leather finishing; it is also used at certain concentrations in colour matching. Finishing components which bond physically to the leather surface can be easily extracted with the help of solutions ^{9, 11, 19, 21}.

The highest concentration of heavy metals detected in bootee leathers was chromium. This high concentration is due to tanning processes, which are carried out predominantly with basic chromium sulphates ^{22, 23}. Depending on the process factors in effect, chromium salts added to the leathers may either form polynuclear cross-links between carboxyl groups of the collagen molecules, or remain suspended form between fibres. It is a known fact that suspended chromium is easily leachable ^{24, 25}. For sufficient physical strength and performance of the finished leathers, a minimum of 2.5 % Cr₂O₃ concentration is needed, which is equal to at least 17 100 ppm of chromium, calculated according to atomic masses of oxygen and chromium ²⁶. The total chromium contents of chromium tanned and semi-chromium tanned baby bootee leathers were detected as 29613.75 ppm and 14405.25 ppm, respectively. In contrast, the chromium content of the chromium-free tanned garment leathers was determined to be only 0.23 ppm.

Lead contents were found to be lower than the limit value of 90 ppm given in BS EN 71-3 (1995) for children's bootee leathers. When results of lead analysis in all samples were compared with the limit value of 0.8 mg/kg suggested in SG list, leachable amounts of lead for all leathers were found to be higher than SG limit values ¹⁵.

Lead is believed to accumulate in animal skins from sources of lead in their natural environments during their lifetime and after slaughtering. In addition to this, the use of the lead chromate based pigments called chrome yellow in preparation of pale or nuanced colours and colour matching during the finishing processes is understood to be the primary source of lead ^{25, 27, 29}.

The limit value given in BS EN 71-3 (1995) for mercury concentrations in children garments which are in contact with the skin is 60 ppm, and the limit value for leachable mercury concentrations given in SG criteria list is 0.02 mg/kg ¹⁵. In the study, mercury concentrations in leather samples were found to be higher than the limit values given in the SG list. However, the leachable mercury was detected at low levels in samples according to BS EN 71-3 (1995) limit values. This mercury content may be derived from fungicides and biocides ^{16, 30}.

The amount of selenium leachable in acid solution was lower than limit values of 500 mg/kg ². Selenium is used widely in vitamin preparations and livestock feeds. The low selenium concentrations determined in finished bootee leathers might have accumulated during the period when the animal was alive due to bioaccumulation as animal took these metals from in different sources.

Conclusion

In conclusion, our study focused on the detection of potential hazardous substances in goods which children are in contact with in their daily lives; these were leathers and leather products, whose production involves the intensive use of metal salts.

It is extremely important that all the materials contain only a low quantity of harmful substances or, if possible none at all. However; when it comes to leather goods, this is neither a realistic view nor an applicable practice. It is a very well-known fact that leather and fur must be tanned and dyed with chemicals to achieve the desired characteristics. Thus, in this process it would not be possible to avoid chemicals entirely.

It was found that the heavy metal content of bootee leathers was generally dependent on the use of chemicals in production. The chromium content of leathers was found to be high, due to its large consumption in the tanning process. Antimony, arsenic, barium, cadmium, lead, mercury and selenium were found, but at quite low levels, and these were thought to have been introduced into the leather structures physically and chemically during the processing.

There are various standards which have been set for heavy metal contents; the limits for a particular metal are set by orders of magnitude for different authorities. At the moment, the limits of the EN 71 standard are approved in terms of health and commerce. Moreover, the SG limits that are seen as the signs of low-pollutant leather products have been raised by some authorities. This situation shows us that in the future, the pressure of the academic world against environmental pollution and threats on human life will grow stronger. In accordance to this, the ideals like SG which seem like impossible or impracticable will be the ultimate standards. Thus, the leather companies have to use ecological products as much as they can in the production process.

Interest in the heavy metal content of ecological textile has been increasing recently. It is likely that investigations concerning ecological textile will expand in the future and will include leather goods as well. Babies' skins are more sensitivity to heavy metals, which they come into contact with from goods which have a high concentration. For this reason, leather process recipes for baby goods should be revised, and leathers for baby goods should be processed using ecological methods. In addition, it is recommended that consumers should wear socks which possess a barrier against direct contact of human skin with the leather surface in the shoes to avoid easily absorption of the some heavy metal ions. Shoes should not be dried on sunshine when getting wet and cured with alkali shoe creams to avoid oxidations of chromium.

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