Survey of Chemical Substances in Consumer Products

Survey no. 3, 2002

Investigation of the Content of Cr(VI) and Cr(III) in Leather Products on the Danish Market

Stefan Rydin, Danish Technological Institute, Environment

Table of contents

SUMMARY	5
1 BACKGROUND AND INTERNATIONAL EX	KPERIENCES 6
1.1 BACKGROUND	6
1.2 ECO-LABELS AND LEGISLATION	7
2 ANALYTICAL METHODS	8
3 CHROMIUM(VI) AND CHROMIUM(III) IN I DANISH MARKET	PRODUCTS ON THE 11
3.1 Supplementary analyses of baby-shoes 3.1.1 Discussion of results	14 14
4 AMOUNTS AND ORIGIN OF LEATHER PR	ODUCTS ON THE
DANISH MARKET	16
4.1 DANISH IMPORT AND EXPORT	16
4.2 WORLD-WIDE PRODUCTION OF LEATHER	17
4.2.1 Heavy Leather from Bovine Animals	17
4.2.2 Light leather from Bovine Animals	18
4.2.3 Leather from Goats and Sheep	18
5 REFERENCES	19

Summary

The Danish Environmental Agency initiated in April 2001 an investigation to evaluate the possible content of hexavalent and trivalent chromium in leather products on the Danish Market. Forty-three leather products were purchased in Denmark and the leather was analysed for its content of hexavalent chromium and total chromium. The products represented ten different product groups (watch-straps, shoes, gloves, baby-shoes, working gloves, leather jackets, trousers, leather-tops, skirts and leather-hats).

Fifteen out of the forty-three of the-leather products contained hexavalent chromium in levels above the detection limit of 3 mg/kg. Hence, thirty-five (35%) of the products contained hexavalent chromium. In the 15 products where hexavalent chromium was detected, the concentration range was from 3,6 to 14,7 mg/kg (analysed according to DIN 53315).

Additionally ten baby-shoes were analysed for its content of hexavalent chromium. The content of hexavalent chromium was below the detection limit in all samples. Two of the baby-shoes were also analysed for migration of chromium according to the European Standards on safety of Toys, EN 71 Part 3. Both the upper leather and the sole leather were analysed separately. All four samples showed a migration higher than the stated safety requirement of the EN 71. The migration of chromium found in the samples was between 370-980 mg/kg Cr.

The number of leather products containing hexavalent chromium was not expected, especially taking into consideration that it relatively easy and well known to produce leather, which do not contain any hexavalent chromium.

1 Background and international experiences

1.1 Background

The Danish Environmental Agency initiated in April 2001 an investigation of the possible content of hexavalent and trivalent chromium in leather products on the Danish Market. The background was that hexavalent chromium compounds are characterised as either Carc. cat. 1 (chromium(VI)trioxid) or Carc. Cat. 2 (other hexavalent chromium compounds; Danish EPA 2000) , and R43 (may cause sensitisation by skin contact). The investigation was initiated in order to assess the content of hexavalent chromium in a selection of leather products and to identify the levels of eventual hexavalent chromium in the leather.

Chrome tanning is the most important tanning method for the leather industry and represents over 80% of the leather production world-wide. The chemical that is used in tanning processes is a basic chromium(III) sulphate. Hexavalent chromium is not used in the tanning process and has no tanning effect.

However, during the last years analysis of leather articles has shown traces of hexavalent chromium (Hauber and Germann 1999; Graf, 2001). This was unexpected since chromium(VI) in the presence of a high proportion of organic matter and low pH in the leather is unstable and is expected to be reduced to chrome(III) (Hauber and Germann 1999).

The issue of chrome (VI) in leather started to develop around 1994-1995, when hexavalent chrome was found in leather articles. The first findings were made in a French study (Martinetti 1994) and very soon after the same results were seen in Germany (Hauber and Germann 1999).

As a consequence of these analytical results, several research activities started up, especially in Germany (Graf 2001). The research focussed on why hexavalent chromium could be present in leather and also how it could be avoided during the leather manufacturing. The major chemical suppliers, in co-operation with the German Leather Institute in Reutlingen, carried out a thorough study of the subject and were able to identify which process steps were critical. Furthermore it was possible to identify means on how to avoid hexavalent chromium in leather.

The problem with hexavalent chromium in leather can be avoided by using the correct processes and all information on this are available both through the leading chemical suppliers to the leather industry (TEGEWA 1997) and through several publications in international leather journals (Hauber and Germann 1999). Overall, the available information from the chemical suppliers to the leather industry and literature clearly suggests that there is no reason for producing leather containing hexavalent chromium (Graf 2001).

No public survey of the presence of hexavalent chromium in leather products has been done previously. Several test-laboratories carry out a number of analyses on hexavalent chromium on leather products, but it is mainly when a buyer suspects that the leather contains hexavalent chromium that the analysis is made. Another reason for analysing leathers for hexavalent chromium is when the producer needs a certificate stating that the leather does not contain hexavalent chromium. It is therefore difficult to get any statistics of the magnitude of the problem in Europe.

1.2 Eco-Labels and legislation

Germany was the first country to implement legislation related to the content of hexavalent chromium in leather. The revised version of the Food and Commodities Act dated 8th July 1993 §30 forbids commodities that are causing adverse health effects by toxicological effective substances. According to this regulation chromium(VI) compounds must not be detectable in leather (Haidle 2001). The German legislation use DIN 53314 as analytical method (detection limit 3mg/kg).

No other country has introduced legislation on the content of hexavalent chromium in leather. However, there are several eco-labelling schemes for leather products and leather and many of them have introduced limit values for hexavalent chromium in leather. An overview of eco-labelling schemes having limit values for hexavalent chromium are found in Table 1.1.

Table 1.1
List of ECO-label schemes limit values for hexavalent chrome in leather

Country	Organisation	Name	Year	Limit value of Cr(VI), mg/kg	Analytical Method's detection limit
International	International Council of Tanners	Eco-Tox Label	1996	5	IUC 18 (3 mg/kg)
Germany	*	SG (Schadstoffgeprüft)	1997	Not detectable	DIN 53314 (3 mg/kg)
Germany	Lederinstitut Gerberschule Reutlingen	Test Mark for Leather	1997	Below detection limit (DIN 53314)	DIN 53314 (3 mg/kg)
European Union	EU	Community Eco-Label for footwear (Flower)	1999	10	EN 420 (2 mg/kg)
International	TESTEX	Öko-Tex Standard 100	2000	Below detection limit (0.5 ppm)	Öko-Tex method** (0.5 ppm)
Catalonia	Department de Medi Ambienti	Distintiú de garantia de qualitat ambiental	2000	5	IUC 18 (3 mg/kg)
Brazil	Associação Brasileira de Normas Técnicas	Marca ABNT- Qualidade Ambiental (footwear)	1999	3	DIN 53314 (3 mg/kg)

^{*} Prüf und Schuhforaschungsinstitut Pirmasens; TÜV Rheinland Sicherheit und Umweltschutz GmbH; Institut Fresenius

^{**} Not available to the public

2 Analytical Methods

At the moment, there exist four official methods for the analysis of Cr(VI). These are DS/EN 420 (from 1994 for glove leather), DIN 53314 (from 1996), IUC 18 (from 1995 but revised 1996) and SLC 22 (identical with IUC 18). The methods are based on the same principle (colourometric analyses using diphenyl carbazide).

Furthermore, there are at the moment, in the Comité Européen de Normalisation (CEN TC 289, WG2, TG1), work going on to develop a general test method for hexavalent chromium in leather. This method is based on the same principle (colourometric analyses using diphenyl carbazide), but includes also an additional step to decolour the extracts in order to avoid any problems with extracted dyestuffs. The draft CEN-method (ENV WI00289055) has gone through the public enquiry stage (November 2001) and the next step will be to discuss the comments, which have been received. One point of discussion is the detection limit, where the current draft proposal states: "The method described is suitable to quantify the Chromium VI content in leathers down to 10 mg/kg and is suitable to show whether a leather complies with the criteria "maximum 10 mg/kg" as it is given e.g. by the Commission decision of 17 February 1999 for the ecological criteria for ecolabel of footwear".

The four testmethods mentioned in the beginning of this chapter are very similar to each other. The DIN-method, IUC-method and the SLC-method are identical and only the DS/EN 420-method contains minor modifications. The DS/EN 420-method consist of two parts where part one is a spot test to detect hexavalent chrome and part 2 is the quantitative determination of hexavalent chrome. The comments below relate to the second part of the DS/EN 420-method.

In the DIN, IUC and SLC-method, the chromium(VI) is extracted from 2 g of a finely cut-up leather sample with a dipotassium hydrogen phosphate buffer for three hours. The extraction in the DS/EN 420-method is carried out by cutting 10 g of leather, which is extracted by dipotassium hydrogen phosphate buffer for 2 hours. The volumetric relation between the sample and the extraction media is also different in DS/EN 420 compared to the other methods. The pH of the solution in all test-methods should be between 7.5-8.0. The inert gas argon is used in order to prevent oxidation in the DIN, IUC and SLC-method.

The extracted chromium(VI) is complexed with a diphenylcarbazide solution in acetone (1,5 diphenylcarbazide). Chromium(VI) oxidises 1,5 diphenylcarbazide to 1,5- diphenylcarbazone which gives rise to a red/violet complex with chromium. The degree of spectral absorption (i.e., extinction) of this dye shows a linear relationship to the chromium(VI) concentration and is measured at by a colour photometer at 540 nm (550 nm in the DS/EN 420-method).

It is stated in the DIN, IUC and the SLC-method that the sample is measured for its extinction at 540 nm in a 2 cm cell against a blank solution (consisting

of water, diphenylcarbazide solution and phosphoric acid). Furthermore, another part of the solution containing the sample is treated as in the method but without the addition of diphenylcarbazide solution. The extinction of this solution is measured and the original sample is corrected for this measured value. This correlation for interference is not included in the DS/EN 420-method.

Finally, the recovery rate is determined in the DIN, IUC and SLC-method to provide information about possible matrix effects, which can influence the results.

The DIN, IUC and SLC-method state "A general detection limit can not be given because the detection limit depends also on the intensity of the colour of the extract. In interlab tests it was possible to detect 3 mg/kg without reaching the detection limit". The detection limit for these methods has been stated to be 3 mg/kg in other parts of this report in order to simplify the reading of the report.

The European Standard EN 420 states that the chromium(VI) content in leather gloves shall be less than 2 mg/kg and this is measured by the method described in DS/EN 420.

There have been some discussions about the test methods and some of the critical points have been the presence of coloured extracts, the pH of the extraction and that the methods are not specific enough (Long et al 2000 and Jambunathan 2000).

The extraction of hexavalent chromium is as mentioned above carried out in a buffer at pH 7.5-8.0. In an acidic medium, chromium (VI) compounds are strong oxidising agents and are reduced to chromium (III) compounds. Consequently, chromium (VI) compounds can be formed or obtained only in a neutral to alkaline medium. Some authors (Long et al 2000) have stated that the pH of the buffer medium may give rise to the formation of hexavalent chromium. It should, however, be noted that the pH used in the extraction is similar to the pH of human perspiration.

The problem with coloured extracts are well known and should be avoided by the use of a blank as stipulated in the methods. However, if the colour in the blank is too strong, it may make the sample impossible to analyse.

Furthermore, it should be noted that all four analytical methods have been subject to several interlaboratory tests before they have been approved as official test-methods. The test-methods only require one analysis per sample but the average result of two analyses have been used in this project.

An often-used method in publications about hexavalent chromium is the German DIN-method. There are several reasons for this. The first reason is that Germany is the only country having legislation regarding hexavalent chromium in leather (which refers to the DIN-method). The second reason is that there has been several research activities carried out in Germany initiated by the chemical industry (a major part of the chemical suppliers to the leather industry is based in Germany).

DIN 53314 has been used in this investigation to determine the content of hexavalent chromium in leather. The reason for choosing the DIN-method is

that it is a national standard and applicable for all types of leather. Furthermore, the DS/EN 420-method requires 10 g of sample material while the DIN-method only requires 2 g of sample material. The need for less sample material is an advantage when analysing for example watchstraps where only small quantities of sample material are available.

The analyses of hexavalent chromium in this project were carried out by the German Leather Institute "Lederinstitut Gerberschule Reutlingen" which is accredited for this particular analysis and have major experiences in performing it.

3 Chromium(VI) and Chromium(III) in Products on the Danish Market

The results from the analysis of 43 leather-products are shown below. Forty-five (45) products were bought in the Copenhagen area and 43 of these were analysed for Cr(VI)-content and total chrome-content (two of the samples consisted of artificial leather and were therefore not analysed).

The following products were investigated:

Table 3.1 Analysed products.

Product	Number of Samples	Number of samples containing hexavalent chromium above 3 mg/kg (DIN 53314)
Watch-Strap	5	2
Shoes	5	2
Gloves	5	1
Baby-Shoes	5	1
Working gloves (garden)	5	3
Leather Jackets	8	2
Trousers	5	0
Leather-tops	2	2
Skirts	2	1
Leather-Hat	1	1

Furthermore, two leather balls were purchased for analyses. It was however seen during the cutting of the samples that they were manufactured of artificial leather and they were therefore not analysed in this investigation.

The results from the analyses are showed in the next table. It can be seen from the results that 35% (15 out of 43) of the leather-products contained Cr (VI) in levels above the detection limit of 3 mg/kg.

Table 3.2 Products analysed for its content of hexavalent and total chromium.

Reference	Article	Cr(VI)-content DIN 53 314 in mg/kg*	Total Chrome (AAS)
		(average of two analyses)	in % Cr ₂ O ₃ *
UR 1	Watch-Strap	Below detection limit***	3,1**
UR 2	Watch-Strap	3,6	2,2**
UR 3	Watch-strap	Below detection limit	2,8**
UR 4	Watch-strap	Below detection limit	2,5**
UR 5	Watch-strap	3,7	4,0
SK 1	Shoe	10,4	2,0
SK 2	Shoe	Below detection limit	3,3
SK 3	Shoe	Below detection limit	3,9
SK 4	Shoe	Below detection limit	2,7
SK 5	Shoe	6,3	4,2
HA 1	Gloves	Black leather –below det.li. Lining - 8,6	2,6 2,8
HA 2	Gloves	Below detection limit	4,6
HA 3	Gloves	Below detection limit	3,3
HA 4	Gloves	Below detection limit	3,6
HA 5	Gloves	Below detection limit	5,6
BS 1	Baby-shoe (sandals)	Below detection limit	3,2
BS 2	Baby-shoe (sandals)	Below detection limit	3,2
BS 3	Baby-shoe (sandals)	Below detection limit	4,0
BS 4	Baby-shoe	6,4	3,8
BS 5	Baby-shoe	Below detection limit	5,0
TH 1	Working gloves (garden)	14,7	3,8
TH 2	Working gloves (garden)	4,0	2,7
TH 3	Working gloves (garden)	6,2	4,9
TH 4	Working gloves (garden)	Below detection limit	4,1
TH 5	Working gloves (garden)	Below detection limit	5,2
JA 1	Jacket	Below detection limit	5,2
JA 2	Jacket	Below detection limit	1,8
JA 3	Jacket	Below detection limit	5,6
JA 4	Jacket	Below detection limit	5,5
JA 5	Jacket	10,6	4,2
JA 6	Jacket	Below detection limit	3,2
JA 7	Jacket	6,8	3,3
JA 8	Jacket	Below detection limit	4,4
BU 1	Trousers	Below detection limit	3,8
BU 2	Trousers	Below detection limit	2,5
BU 3	Trousers	Below detection limit	5,1
BU 4	Trousers	Below detection limit	4,7
BU 5	Trousers	Below detection limit	3,7
AN 1	Leather-top	4,9	5,4
AN 2	Leather top	5,0	4,2
KJ 1	Skirt	Below detection limit	4,7
KJ 2	Skirt	8,5	4,8
HT 1	Hat	9,1	4,9

Calculated as dry weight leather (Water content determined according to DIN 53 304)

Not calculated as dry weight leather (due to small amount of sample material)

Detection limit = 3 mg/kg

The number of leather samples, which contain hexavalent chromium was unexpected, especially taking into consideration that hexavalent chromium can be avoided by relatively simple process changes.

It can be noted that BS 4 (baby-shoe) is a home-shoe for babies. Since babies can be expected to suck on their shoes, they can potentially be exposed to Cr (VI). Due to the finding of hexavalent chrome in BS 4, additionally ten baby home-shoes were purchased and analysed for its content of hexavalent chrome. Furthermore, two of the shoes were analysed for migration of chromium. The results can be seen in the tables in section 3.1.

Three out of five working gloves contained hexavalent chromium. Working gloves are quite often low-cost products, and the process conditions and chemicals (especially fatliquors) that in some cases are used have been shown to increase the risk for the formation of hexavalent chromium in the leather (Hauber and Germann 1999). The product is expected to be in contact with the human skin when it is used.

The occurrence of hexavalent chromium in two out of five watch-straps is high. The products are used every day by the consumer and are obviously expected to be in constant contact with the human skin.

Two leather tops have been analysed and both contained hexavalent chromium. This product type is also expected to be in constant contact with the human skin.

Two out of five shoes contained hexavalent chromium. There are today around 200-300 new cases of severe chromium allergy every year due to footwear in Denmark (Menne 2001). Shoes are normally not in direct contact with the human skin, although it may occur in e.g. shoes for ladies and in sandals.

One out of five pair of gloves contained hexavalent chromium. The gloves are obviously expected to have direct skin contact.

Two out of eight leather-jackets contained hexavalent chromium. This is slightly below the average in the investigation, but still a high figure (25%). The jackets are normally not in contact with the human skin when they are used.

None of the five tested leather trousers contained hexavalent chromium.

One out of two leather skirts contained hexavalent chromium and the only leather-hat, which was tested contained hexavalent chromium. The leather hat is expected to be in contact with the human skin/hair when it is used. The leather skirts are expected to often be in contact with the human skin when they are used.

The content of chromium (III) has been analysed as the total chromium content in the leather samples Eventual hexavalent chromium in the products will also be included in these figure, but the content of hexavalent chrome is negligible in relation to the content of chromium (III). The concentration is expressed as % $\rm Cr_2O_3$, which is the normal unit in the leather industry. The content of chromium in leather depends on the product, but will normally be between 3-5% of $\rm Cr_2O_3$. The chromium content should generally not be below

2,5% Cr₂O₃ for chrome tanned leather in order to receiving a good quality of the leather (UNIDO 1994).

3.1 Supplementary analyses of baby-shoes

Additionally ten baby shoes similar to BS 4 (containing hexavalent chromium) were purchased and sent to analyses for hexavalent chrome and chrome content. Four of the shoes had the same red colour as BS 4. Two of these shoes were analysed for migration of chromium according to DS/EN 71 part 3:Dec 1994. The results follows in the Table 3.3 and Table 3.4.

Table 3.3 Analysis of baby shoes

Reference	Article	Cr(VI)-content DIN 53 314 in mg/kg* (average of two analyses)	Total Chrome (AAS) in % Cr ₂ O ₃ *
BS 6	Dobyoboo	Below detection limit	17
	Baby-shoe		4,7
BS 7	Baby-shoe	Below detection limit	4,8
BS 8	Baby-shoe	Below detection limit	4,9
BS 9	Baby-shoe	Below detection limit	4,6
BS 10	Baby-shoe	Below detection limit	4,5
BS 11	Baby-shoe	Below detection limit	5,2
BS 12	Baby-shoe	Below detection limit	3,9
BS 13	Baby-shoe	Below detection limit	3,7
BS 14	Baby-shoe	Below detection limit	4,5
BS 15	Baby-shoe	Below detection limit	4,4

As previously mentioned, two of the samples were analysed for migration of chromium according to DS/EN 71 part 3:Dec 1994- Migration of certain elements. ICP-AES was used as detection method. The sole and the upper leather from the shoes were analysed separately. The results follows in the table 5.2.

Table 3.4 Analysis of of sole and upper leather.

	Migration of elements found (mg/kg)							
Material	Sb	As	Ba	Cd	Cr	Pb	Hg	Se
BS 13 – Sole	<6	<2.5	<25	<7.5	430	< 9	<6	<50
BS 13 – Upper	<6	<2.5	<25	<7.5	560	< 9	<6	<50
BS 14 – Sole	<6	< 2.5	<25	<7.5	980	<9	<6	<50
BS 14 – Upper	<6	< 2.5	<25	<7.5	370	< 9	<6	<50
Limits * DS/EN 71-3		Limits for migration of elements from material (mg/kg)						
	60	25	1000	75	60	90	60	500

The limits are not part of the test results and are only quoted for reference.

It can be seen that the samples do not comply with the stated safety requirements of the European Standard on Safety of Toys EN 71 Part 3:Dec.1994 2.rev.

3.1.1 Discussion of results

The shoe BS 4 was identical in colour and type to BS 12-BS15. It can be seen from the results that BS 4 contained hexavalent chromium (6,4 mg/kg), while BS 12-BS 15 did not contain hexavalent chromium (above the detection limit of 3mg/kg). However, the shoes were bought at different occasions and a

visual inspection of the samples BS 12-BS 15, showed that the shade of the colours were not completely identical. International studies (Graf 2001; Hauber C and Germann 1999) have shown that the most critical processes in leather manufacturing are the wet aftertreatments which comprises neutralisation, dyeing, fatliquoring and retanning. Small changes in these processes between different batches of leather may therefore be a reason for finding hexavalent chromium in one batch while another batch may not contain hexavalent chromium.

Furthermore, there are large variations in the migration of chromium from the shoes (BS13 and BS 14) and also from the sole and upper leather of the shoe. A visual inspection of the shoes clearly shows that the sole and the upper leather are different types of leather. The sole leather is suede leather while the upper leather is grain leather. Furthermore, it is a difference in the shade of the colour in the sole leather and the upper leather. This explains the difference in migration of chromium from the sole and the upper from the same shoe.

4 Amounts and Origin of Leather Products on the Danish Market

It is of interest to know where the leather on the Danish market has been produced, especially if a correlation between the occurrence of hexavalent chromium in leather and the country of origin can be found. The present investigation does not comprise enough samples to determine eventual correlation between origin of the leather and content of hexavalent chromium.

Leather is in general not a consumer product, although some shop sells leather directly to consumers. It is therefore not easy to identify the origin of the leather, since shoe manufacturers, clothing factories etc in many cases will buy the leather from other countries and the origin of the leather could be from any part of the world. The label that a product comes from a certain country does not necessary say that the leather origins from the same country. Denmark has for instance a production of shoes of around 10 millions pair per year, but no shoe upper leather are produced in Denmark.

Another aspect that makes the identification of the origin of the leather difficult is that part of the leather manufacturing may take place in one country while the final leather production processes takes place in another country.

Furthermore, for a consumer it is even more difficult to find out where the leather is coming from, since many products do not have any information on where the product is made (especially common for leather clothing)

One sources for statistical information on leather and leather products is the FAO statistical compendium for raw hides and skins, leather and leather footwear, which includes information on the production of leather and shoes and the trade from 1979-1997. Another source is the Danish Statistics (Danmarks Statistik) about external Trade by Commodities and countries, which gives information on which countries the leather products on the Danish Market are imported from.

4.1 Danish import and export

Some examples of leather products and the import to Denmark follows below. Furthermore, the main countries where the products are coming from are listed below (Danmarks Statistik 2000).

Table 4.1 Import and export of leather products to and from Denmark.

Leather	Import	Export	Major Countries w	here Denmark import the	
Product			product from		
Shoes	15 Mill. pairs	8.250 Mill.	Portugal	3.260.000 pairs	
	•	pairs	Thailand	1.275.000 pairs	
			Slovakia	880.000 pairs	
			China	765.000 pairs	
			Vietnam	700.000 pairs	
			Spain	415.000 pairs	
Clothing	1225 tonnes	587 tonnes	India	492 tonnes	
			China	492 tonnes	
			Pakistan	290 tonnes	
			Germany	77 tonnes	
			Tyrkey	59 tonnes	
Working	10.329.058	4.691.709	Kina	8.310.741 pairs (1358 t)	
Gloves	pairs (1625	pairs (771	Pakistan	314.663 pairs (55 t)	
	tonnes)	tonnes)	India	873.122 pairs (82 t)	
Gloves	756.468	65610 pairs	China	516.370 pairs (64 tonnes)	
	pairs (106 tonnes	(13 tonnes)	Pakistan	57.997 pairs (9,4 tonnes)	
Leather	244 tonnes	147 tonnes	Thailand	62,4 tonnes	
Articles	244 (0111165	147 torries	China	53,6 tonnes	
VI IICIE2			The Netherlands	32,6 tonnes	

4.2 World-wide production of leather

The main producing countries of different types of leather world-wide in 1996 is given below (FAO, 1998):

4.2.1 Heavy Leather from Bovine Animals

(wet-blue, crust, finished)

The term heavy leather refers to thick leather (usually thicker than 2.5 mm) and is generally understood as vegetable-tanned sole, belting, strap and mechanical leathers made from unsplit cattle hides. Heavy leather is sold by weight.

Table 4.2 Heayv leather from Bovine dyr (wet-blue, crust, finished)

	(Wet-blue, crust, firitsfied)					
10 largest-	Production in					
	19	996				
producing countires	1.000	% total				
	ton					
China	103.00	21.64				
	0					
Ex-USSR	80.000	16.66				
Italy	55.000	11.46				
India	52.700	10.98				
USA	35.000	7.29				
Brasil	24.600	5.12				
Argentina	18.500	3.85				
Turkey	16.000	3.33				
Syd Korea	13.000	2.71				
Egypt	8.900	1.85				

4.2.2 Light leather from Bovine Animals

(wet-blue, crust, finished)

The term light leather refers to thin leather (thickness usually lower than $1.5\,$ mm) and is sold by area.

Table 4.3 Light leather from Bovine aminals (wet-blue, crust, finished)

10 largest-	Production in 1996	
producing countires	1.000 ton	% total
Italy	155.500	16.06
Syd Korea	133.779	13.82
China	95.940	9.91
Ex-USSR	55.741	5.76
India	52.211	5.39
Brasil	46.841	4.84
USA	41.638	4.30
Mexico	37.161	3.84
Spain	29.728	3.07
Argentina	27,871	2.88%

4.2.3 Leather from Goats and Sheep

(wet-blue,crust, finished)

Table 4.4 Leather from goats and sheeps (wet-blue, crust, finished)

10 largest-	Production in	
	19	996
producing countires	1.000	% total
·	ton	
China	82,534	20.68%
India	60,470	15.15%
Italy	39,000	9.77%
Turkey	26,663	6.68%
Spain	20,903	5.24%
Ex-USSR	18,580	4.65%
Pakistan	16,007	4.01%
United Kingdom	9,690	2.43%
France	8,798	2.20%
USA	7,525	1.89%

5 References

Danish EPA, List of undesirable substances, Environmental review No. 15, 2000

Danmarks Statistik, Udenrigeshandeln fordelt på varer og lande 2000 (External Trade by commodities and countries), 2001

DIN 53314, Bestimmung des Chrome(VI)-Gehaltes in Ledern, 1996

DS/EN 420, General requirements for gloves, 1994

EN 71 Part 3:Dec.1994 2.rev. (Migration of Certain Elements), European Standard on Safety of Toys

FAO World Statistical compendium for raw hides and skins, leather and leather footwear 1979-1997, 1998

Graf D, Formation of Cr(VI) traces in chrome-tanned leather: causes, prevention & latest findings, JALCA, May 2001, 96(5), 169

Graf D, The formation of chrome (VI), Leather, November 2000, 202 (4705), 58

Haidle W, Personal Communication, 2001

Hauber C and Germann H-P, Investigations on a possible formation and avoidance of chromate in leather, World Leather, October 1999, 12(6), 73

Hauber C and Germann H-P, Untersuchen zur Entstehung und Vermeidung von Chromat in Leder, Leder & Haüte Markt 1999, 9, 25

IULTCS Chemical Test method: Determination of Chromium VI Content (IUC 18), J.Soc.Leather Technol.Chem. May-June 1997, 81(3), 109

Jambunathan S and Dasgupta PK, Determination of hexavalent chromium in leather extracts by the Diphenylcarbazide (IUC-18) procedure: Pitfalls and Refinements, JSLTCS, March-April 2000, 84(2), 63

Long AJ, Cory NJ and Wood CB, Potential chemical mechanisms causing false positive results in hexavalent chromium determination, JSLTCS, March-April 2000, 84(2), 74

Martinetti R, Thesis "Contribution à la labellisation 'écoproduit' de cuirs tannés aux sels de Chrome: étude de la mobilité du Chrome", Lyon-France:CTC 27 October 1994

Menné T, Personal communication (2001)

SLTC Chemical Test method: Determination of Chromium VI Content (SLC 22), J.Soc.Leather Technol.Chem. May-June 1997, 81(3), 109

TEGEWA, Recommendations of the TEGEWA Association to avoid chromium (VI), August 1997

 $\label{lem:eq:control} \begin{tabular}{l} UNIDO, Acceptable Quality Standards in the Leather and Footwear Industry, 1984 \end{tabular}$