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Distribution of Cr (III) and Cr (VI) in chrome tanned leather

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Basic chromium sulphate is the most versatile and common tanning agent in the leather industry. Under certain circumstances, the oxidation of the trivalent chromium salts into the hexavalent compounds, which are used in leather manufacture, is a crucial issue. In this study, different proportions of basic chromium sulphate were used in tanning and re-tanning processes according to a commonly used recipe, and levels of chromium oxide and hexavalent chromium were studied stratigraphically in the cross-section of the leather. It was observed that the levels of chromium oxide and hexavalent chromium in the skins increased in relation to the proportions of basic chromium sulphate used in the process, and that the amounts added in the tanning process had a greater effect on the levels of hexavalent chromium formed in the layers of the skins than did the amounts added in re-tanning.

Keywords: Skin, Tanning, Chromium oxide, Chromium (VI), Tanned leather

The leather manufacturing industry processes raw skins and hides for various purposes. Raw skins are transformed into stable finished products by a series of chemical and mechanical processes[1,2]. Among these processes, tanning is very importance. In the leather industry, tanning means the conversion of raw skin into finished leather through various technical processes[3]. Unless the tanning process is carried out, the raw skin protein, which is made of collagen, will putrefy and progressively deteriorate[4]. The collagen proteins will deform when heated, and in water they will turn into gelatine[5]. Thus, tanning is an essential process for the conversion of the collagens in natural skin and hides into a stable form, giving the material individual durability by allowing the penetration of various tanning agents with different characteristics into the structure through mechanical action in floats and by reaction with reactive groups of collagens[1,3,5]. Tanning agents are not only used in the tanning process, but they can also be used in another stage, which is called re-tanning/retannage, to further achieve the final features[5].

Now-a-days the use of chromium has accelerated in the leather industry as it enables faster and cheaper production of highly resistant and durable leathers[6,7]. Today, more than 80% of finished goods are tanned using basic chromium salts[8,9]. However, high *p*H value, temperature, UV lights, unsuitable storage conditions and the effect of using lubricants with double bonds in the molecule during production, possibly turn up the oxidation of the trivalent chromium into the hexavalent form[10-16]. For this reason, a limit of 3-50 ppm has been imposed by various countries on the level of Cr (VI) in leather[13].

Since 1994, when the formation of chromate complexes in leather goods was identified, strong pressure has been put on the global leather industry by both consumers' rights associations and environmental protection organisations[17] to reduce its content in the leather. This has had a great effect on leather exporting countries, and many researches have been devoted to this subject. Studies have been undertaken for identifying the factors responsible for oxidation, reducing or completely eliminating the use of chromium in tanning, the determination of hexavalent chromium in the leather, and problems related to analysis methods[18-21]. It is likely that chromium tanning will be in use for years to come because of the characteristics it imparts to final products and its ease of application. This study examined the stratigraphic distribution of 3- and 6-valent chromium compounds in the leather, and determined the relation between the amount of chromium used in tanning and the formation of hexavalent chromium in the leather.

Experimental Procedure

Materials

Eighteen standard quality commercially pickled sheep skins with a thickness of 1.0-1.2 mm and a *p*H value of 2.0 were used. Because of their bilateral features, these skins were cut into two equal parts down their backbones[22]. The experiments were carried out on 36 sides obtained in this way.

Tanning of skins

The sides were divided into 3 groups and these groups were tanned with 33% basic chromium sulphate in proportions of 4, 6 and 8%. Subsequently,

the skin groups were divided into 3 sub-groups and chromium re-tanning was carried out by adding 33% basic chromium sulphate in proportions of 2, 4 and 6%. The process recipes are given in Tables 1 and 2.

After the tanning and re-tanning, the skins were stored for 6 months and then divided into three layers in a splitting machine to determine the distribution of 3- and 6-valent chromium compounds.

Analyses

The trivalent chromium content in the leathers ripped horizontally into layers by the splitting process was analyzed in each split layer according to IUC/8[23], and hexavalent chromium was determined according to DIN 53314 (IUC 18)[24,25]. The calibration curve of the standard solutions prepared for the determination of chromium according to the DIN 53314 method is given in Fig. 1.

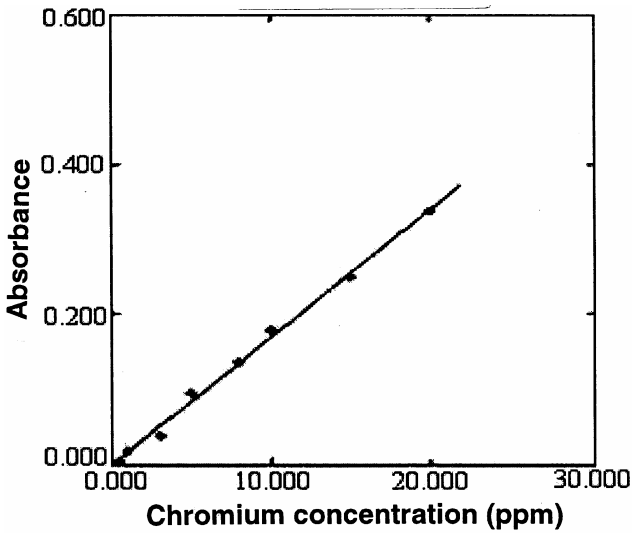

Fig. 1—Calibration curve of standardized solutions

Table 1—Tanning recipe

Process	Additives	Temp. (°C)	Prop.(%)	Time (min)	Remarks
Depickling	Water	25	200	20	7 °Bé Brine solution
	Acid bating agent		1	30	
	Sodium formate		0.5	30	
	Sodium bicarbonate		1	45	*p*H: 5.5 / Keep overnight
Fleshing					
Degreasing	Alkyl polyglycol ether		3	120	Drain
Washing	Water	35	200	20	Drain
Washing	Water	35	200	20	Drain
Pickling	Water		150	20	6° Bé
	Formic acid		4.0	40	
	Sulphuric acid		0.5	60	*p*H : 2.9
Tanning	Basic chromium sulphate		X	240	X= 4, 6 and 8%
	Sodium formate		1	40	
	Sodium bicarbonate		0.8	60	
	Sodium bicarbonate		1.0	20	*p*H: 3.8, Drain
Washing	Water	25	200	30	Drain, horse up (3 days)

Table 2—Re-tanning recipe

Washing	Water	35	300		
	Formic acid		0.3		
	Alkyl polyglycol ether		0.3	30	Drain
Washing	Water	35	300	10	Drain
Re-tanning	Water	32	150		
	Aliphatic dicarboxylic acid salts		0.5	30	
	Basic chromium sulphate		X	240	X= 2, 4 and 6 %
	Phenol sulphonic acid condensate		2	30	
	Sodium formate		0.5	15	
	Sodium bicarbonate		0.5	15	*p*H: 4.2
	Naphtalene sulphonic acid condensate		2	30	
	Formic acid		0.5	30	Drain
Washing	Water	25	200	20	Drain

Results and Discussion

Distribution of the proportions of chromium oxide (Cr_2O_3) and Cr (VI) in the lower, middle and upper parts of the split leathers are given in Table 3. From the results it can be seen that the maximum chromium oxide amounts were found in the lower split part of the leathers, and the amounts decreased towards the upper split parts. When the effect of basic chromium sulphate proportion was observed, it was found that the maximum chromium oxide concentration was found when 6% basic chromium sulphate was used, and the minimum chromium oxide contents resulted from the addition of 2% basic chromium sulphate. These results indicated that when the basic chromium sulphate concentration added to the skins is increased, the chromium oxide content of leather also increases.

In terms of providing the performance characteristics satisfactorily, it is recommended that chrome tanned leathers should include a minimum of 2.5% chromium oxide[26]. Unless an appropriate

Table 3—Distribution of Cr_2O_3 and Cr (VI) in the sections of leather layers

Leather Layer	Chrome added in tanning (%)	Chrome added in re-tanning (%)	Cr_2O_3 determined (%)		Cr(VI) determined (ppm)	
			Mean	Average SD	Mean	Average SD
Lower	4	2	3.57		7.14	
	4	4	3.74	0.17	7.73	0.62
	4	6	3.90		8.39	
Lower	6	2	3.85		7.79	
	6	4	3.94	0.14	8.58	0.83
	6	6	4.12		9.45	
Lower	8	2			10.57	
	8		3.94			
	8	4	4.18	0.16	11.24	0.52
		6			11.59	
			4.25			
Middle	4	2	3.29		6.76	
	4	4	3.43	0.11	6.74	0.77
	4	6	3.50		8.09	
Middle	6	2	3.50		8.49	
	6	4	3.54	6.20	8.82	0.50
	6	6	3.62		9.48	
Middle	8	2			11.45	
	8		3.88			
	8	4	3.93	2.67	11.03	1.44
		6			11.70	
			3.93			
Upper	4	2	3.23		6.38	
	4	4	3.29	7.95	6.71	0.17
	4	6	3.38		6.63	
Upper	6	2	3.32		7.14	
	6	4	3.42	6.53	7.80	0.34
	6	6	3.45		7.59	
Upper	8	2	3.50		7.85	
	8	4	3.57	5.59	8.36	0.37
	8	6	3.61		8.57	

tanning practice is applied, the durability of the finished goods might be unsatisfactory and the hydrothermal stability can be lower than acceptable quality levels. In addition, other undesirable features such as the lacks in appearance and handling problems occur[27]. In this study, the chromium oxide content of the tanned goods was found to be more than the suggested lower limit value.

The maximum hexavalent chromium contents were found in the lower split part of the leathers, whereas the least contents were found in the upper split parts. It was observed that as the amounts of added basic chromium sulphate increased in the tanning process the Cr (VI) contents in the leather also increased. The highest hexavalent chromium levels were found in leathers tanned with 8% basic chromium sulphate, and the lowest hexavalent chromium levels were found in leathers tanned with 4% basic chromium sulphate. It was observed that when the basic chromium sulphate amounts used in re-tanning process were increased from 2 to 6%, the hexavalent chromium contents also increased.

As previously indicated in relevant studies, oxidation to hexavalent form is accelerated by high *p*H values in neutralisation, chemical additives such as ammonia, sodium bicarbonate and free unsaturated fatty acids, exposure of leather to high temperatures (80ºC) and UV light during processes and thereafter. In a study[28] it was observed that more the trivalent chromium used and higher ironing temperature applied, the higher hexavalent chromium level in both fiber and suede side of double-faces were observed.

It was found that the basic chromium sulphate proportions added in tanning had been more effective both on chromium oxide contents and hexavalent chromium formation determined in the each split parts of the leathers than did the basic chromium sulphate proportions added in re-tannage process. It was found that the leathers examined in the study conformed to the EU commission's decision of 18 March 2002 that the hexavalent chromium concentration must not be over 10 ppm in finished leathers[29].

Conclusion

This study reveals that the stratigraphic distribution of chromium oxide contents and hexavalent chromium levels are related to the proportion of chromium sulphate added to the skin in tanning and re-tanning processes. According to the results, the use of 4% basic chromium sulphate is appropriate for both tanning and re-tanning, taking into consideration both the desired qualities of the leather and the formation of hexavalent chromium in the leather.

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