



Relationships in the formation of hexavalent chrome [Cr(VI)]

Renate Meyndt and Heinz-Peter Germann
Lederinstitut Gerberschule Reutlingen (LGR)

Leather research institutes have examined the occurrence of toxic materials in a variety of chrome leathers and leather articles for many years. The Health & Safety department of the German government has shown that some leather goods - such as gloves, shoes and watchstraps - which come into intimate contact with the skin, can contain Cr(VI) in significant quantities. The federal authority has decided in Section 18 of the Consumer Regulations (1) to prohibit Cr(VI) (detection limit of the analytical procedure 3 mg/kg) for leathers in daily use.

Despite extensive researches the origins of the Cr(VI) have not been fully clarified ⁽²⁻⁶⁾. Therefore, there is an urgent need to establish the possible formation mechanisms of chromate in leather and the relationship between extractable total chrome and the risk of skin contact with the user (e.g. wearer of leather shoes and gloves). In addition, the development of safe remedies for use either in leather production or in the manufacture of the leather articles - in particular shoes - as well as in use is required. Final products (e.g. shoes) should not contain Cr(VI) in quantities greater than allowed by regulations. In addition, feasible procedures are needed to durably remove any Cr(VI) content from the leather and intermediates ^(7, 8).

Investigations relating to leather production – presented in this paper – were carried out at LGR.

Investigations regarding the manufacture of leather articles were carried out by the Test & Research Institute Pirmasens (PFI).

The investigation

South German bovine hides were made into shoe upper and lining leather and tested by the following methods:

- Determination of total chrome according to EN ISO 5398-3
- Determination of soluble total chrome using different extraction procedures (EN ISO 17075, EN ISO 17072-1, EN ISO 4098, SG procedure) with final measurement by AAS
- Determination of Cr(VI) by EN ISO 17075
- Test samples were taken where possible according to EN ISO 2418 and the leather and intermediate products were conditioned at 23°C, 50% rH in the dark.

To establish the potential for Cr(VI) formation, the determination of Cr(VI) was carried out after simulated ageing and the results were referred on dry matter (according to EN ISO 4684). The leathers were tested;

- In the original air dried state
- After storage at 80°C for 24 hours in a drying oven at 0-20% rH according to the recommendations of Technical Committee 309 of the shoe industry;
- After exposure in the Xenotest apparatus according to the procedure 3 of the ISO standard ISO 105-B06, 45°C, 65% rH, UV radiation, approx. 48 hrs (controlled by grey scale).

The detection limit of both analytical procedures for Cr(VI) (EN ISO 17075, § 64 LFGB B82.02:2008-10) has been ascertained by round robin tests and is 3 mg Cr(VI)/kg leather. In-house tests on reproducibility have resulted in a lower

detection limit of 0.75 mg Cr(VI)/kg leather. For research purposes only, it was possible to use these in-house detection limits to establish tendencies, illustrated in graphs and tables.

The influence of materials in the original pelt on the formation of Cr(VI)

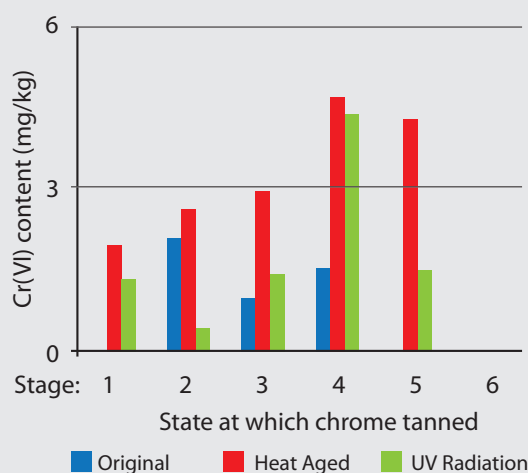
To establish these effects indirectly, hides were processed to five stages identified as key operations before chrome tannage, then chrome tanned at that stage. Each of these different five wet blue produced were then examined for any Cr(VI) content to see if conversion from Cr(III) to Cr(VI) was influenced by materials contained within the original pelt. In addition, a sixth experiment was performed where pure gelatine (i.e. pure collagen where all of the non-collagenous products were absent) was chrome tanned. The five stages selected and the sixth experiment are listed:

- 1] Unlimed pelt (not unhaired).
- 2] Conventionally unhaired/limed, delimed but not bated.
- 3] Conventionally unhaired/limed, delimed and bated.
- 4] Conventionally unhaired/limed followed by intensive white lime, delimed and bated pelt.
- 5] Conventionally unhaired/limed, delimed, bated and intensively degraded.
- 6] Gelatine (i.e. thermally degraded hide collagen)

The findings of this experimental series are presented in *Panel 1*. Each of the five wet blue produced were then divided and processed using two different fatliquors. The leathers were then processed to the crust state as shoe upper and lining leather.



Panel 1: Chrome (VI) content of hides processed to various stages, then chrome tanned

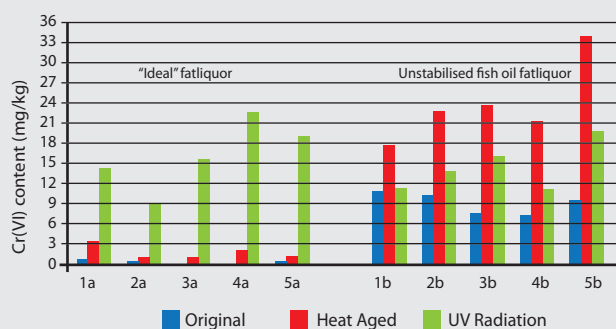


The two fatliquors can be categorised as:

- An “ideal” fatliquor that was expected to be unfavourable to Cr(VI) formation, being based on alkyl-sulfoesters and fish oil derivatives.
- A fatliquor which would facilitate Cr(VI) formation, being based on fish oil.

The results of these test series are presented in *Panel 2*.

Panel 2: Cr (VI) content of crust leather



The results in *Panels 1* and *2* indicated no significant differences between any of the wet blue produced from the five different stages within conventional wet blue manufacture i.e.:

- The materials in the hide had less influence on Cr(VI) formation than heat exposure or UV radiation, the nature of the fatliquor, and the recipe employed respectively.
- The leather fatliquored with the “ideal” fatliquor reacted more strongly to UV radiation than to heat.
- The second fatliquor promoted Cr(VI) formation even in the non-aged leather and more strongly after heat storage than UV radiation.
- The gelatine - which was only processed to the chrome-tanned state - differed from the other variations in that neither heat nor UV radiation led to Cr(VI) formation.

Relationships between total chrome, soluble chrome, and Cr(VI) formation

The determination of total chrome and of Cr(VI) in leather are covered by standards. However, there is no official method for total soluble chrome and it is up to individual test institutes as to which test method is selected.

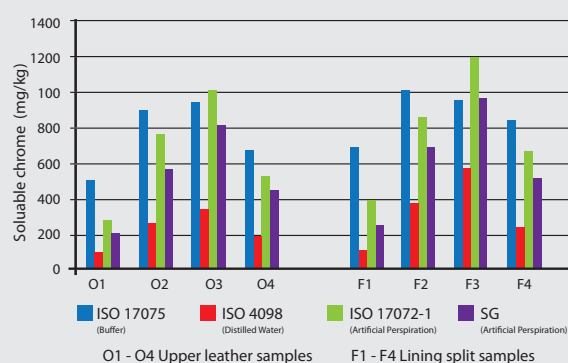
The yield of an extraction is influenced by conditions such as phase relationship, nature of the extracting agent, temperature, time of extraction, pH, etc. The European standardisation committee for leather CEN TC 289 preferred the conditions described in ISO 17072-1 (the present standard). The extraction methods used in this project are specified in *Panel 3*:

Panel 3: Extraction method for total chrome

Procedure	(g) Leather	Extraction Method			Time hr	Temp °C	Stir
		Type	pH	Vol(ml)			
ISO 17075	2	Buffer	8	100	3	room temp	Y
ISO 4098	2	Distilled Water	6	100	4	room temp	Y
prISO 17072-1	2	Artificial Perspiration	5.5	100	4	37	Y
SG-Method	2.5	Artificial Perspiration	5.5	50	4	40	N

The four alternative extractions are compared using upper and lining leathers conventionally produced with an offer of 0.5-2.5% Cr₂O₃ on pelt weight as samples. As expected the various extraction procedures gave different results, with pure water being the least efficient as presented in *Panel 4*.

Panel 4: Soluble total chrome: comparison of extraction methods (4 upper and 4 lining leather samples)



In order to ascertain the relationship between total chrome, soluble chrome and Cr(VI) contents, the leathers produced with different chrome offers were tested in the original state, then after heat ageing and UV exposure. As expected, with increasing chrome offer more chrome was found in the leather. A linear relationship can be seen between total and total soluble chrome but the Cr(VI) content was not affected to any significant extent. In order to compare the results all values have been quoted in mg/kg Cr and the findings are presented in *Panel 5*.

In the case of the shoe upper crust, heat and UV exposure gave no significant increase in Cr(VI), in fact in the case of UV exposure, only a certain tendency could be observed. However,



Panel 5: Leather with increasing total chrome values as Chrome (VI) after heat aging and UV radiation

Sample	mg/kg TS						
	Total Chrome	Soluble Chrome	Cr(VI)	Soluble Chrome	Cr(VI)	Soluable Chrome	Cr(VI)
Upper leather							
1	7335	275	(0.88)	251	(0.78)	257	(1.16)
2	21919	754	<0.75	726	<0.75	744	(1.50)
3	29406	995	<0.75	919	<0.75	1007	(1.92)
Lining leather							
1	10339	383	<0.75	303	(1.78)	325	3.58
2	26532	847	<0.75	779	<0.75	800	6.58
3	36004	1186	<0.75	981	<0.75	1049	7.32

the lining leathers indicated a higher Cr(VI) content after UV exposure. These trials were hence repeated, with similar findings. All of the lining leather from both investigations exceeded the critical value of 3 mg/kg leather (detection limit of the analytical procedure). The experimental variations showed no real relationship between chrome offer (the total chrome content) and the tendency to Cr(VI) formation. The findings of the second test series are presented in *Panel 6*.

Panel 6: Lining leather with increasing chrome content: values as Chrome (VI) after heat aging and UV radiation

Sample	mg/kg TS						
	Total Chrome	Original		After heat aging		After UV Radiation	
		Soluble Chrome	Cr(VI)	Soluble Chrome	Cr(VI)	Soluable Chrome	Cr(VI)
1	10871	240	<0.75	258	(0.86)	374	3.74
2	18584	399	<0.75	228	(1.19)	541	5.59
3	24564	501	<0.75	341	(0.80)	651	4.09
4	28804	471	<0.75	378	<0.75	718	4.48
5	33449	590	<0.75	345	<0.75	685	6.04

Different fatliquors were used in these investigations, but can be categorised as follows:

- The shoe upper leather was fatliquored with a mixture of sulfated oil and one based on synthetic oil.
- The lining leather was fatliquored with a mixture of alkylsulfoester, fish oil derivatives and high molecular aliphatic hydrocarbons.

The fatliquors of both recipes were more sensitive to UV radiation than to heat and drying-out of the leather.

The influence of finishing using alkaline adhesion binders

Samples of the crust shoe upper leathers were finished using various binders, and plated under different conditions. The findings presented in *Panel 7* can be summarised:

- Finishing with an alkaline adhesion binder (aqueous polyacrylate dispersions pH 8.5) caused a certain tendency to Cr(VI) formation due to heat action and increased Cr(VI) values due to UV exposure.

Panel 7: The influence of finishing on Cr(VI) formation

Sample	% Cr ₂ O ₃ on pelt weight	Original	After heat aging	After UV Radiation
Crust upper leather				
	0.5	(0.88)	(0.78)	(1.16)
	1.5	<0.75	<0.75	(1.50)
	2.5	(0.88)	<0.75	(1.92)
	1.5 + fixation	<0.75	<0.75	(1.94)
Finished upper leather				
	0.5	<0.75	(0.97)	2.99
	1.5	<0.75	(1.79)	4.15
	2.5	<0.75	(1.64)	4.17
	1.5 + fixation	(0.90)	(1.79)	4.14

- Other alkaline adhesion binders caused no Cr(VI) formation.
- Variations within plating indicated that the heat energy absorbed was too small to affect even leathers with a tendency to form Cr(VI).

After-treatments for the removal of Cr(VI)

Reductive after-treatments were applied in the float at the end of the retanning/fatliquoring process on the leathers at LGR (also as a spray process at the Test & Research Institute Pirmasens). For this reason, leathers produced on the basis of Cr(VI)-generating recipes were treated in a separate short float with 3% of the reducing chemical agent (ascorbic acid and Product X, which was suitable and already used in practice). No washing step was performed after this treatment.

Analytical tests were carried out two weeks later. These consisted of the determination of total chrome, extractable chrome and Cr(VI). Extractable chrome was analysed in the buffer extract of the Cr(VI) determination procedure.

The results indicate the positive effect of reducing agents. The Cr(VI) content had been reduced below the critical value of 3 mg/kg, whereas the untreated leather exceeded this value.

Comparison of the two reducing agents, indicated that the ascorbic acid was slightly more effective, although the positive effect on Cr(VI) was somewhat reduced by the negative effect on the pH of the leather. Under the experimental conditions, the pH of 3.8 of the control extract was decreased to a critical value of pH 3.2 due to the ascorbic acid treatment.

Panel 8: The influence of after-treatment

Sample	mg/kg TS						
	Total Chrome	Soluble Chrome	Cr(VI)	Soluble Chrome	Cr(VI)	Soluable Chrome	Cr(VI)
Crust upper leather							
original	28391	486	7.05	434	13.05	471	9.39
with ascorbic acid	26249	1524	(0.92)	1517	(1.18)	1517	(0.90)
with product x	28316	791	(1.49)	743	(2.21)	744	(2.12)
Crust lining leather							
original	32267	377	2.98	322	12.89	365	5.98
with ascorbic acid	30239	1904	<0.75	1651	<0.75	1752	<0.75
with product x	29814	870	<0.75	754	(0.84)	833	<0.75



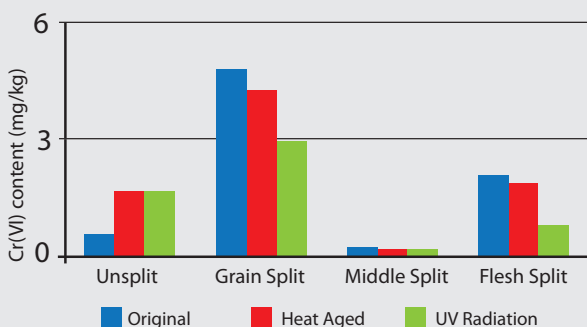
Noteworthy is the effect of the post treatment on total and total extractable chrome content. In comparison with the untreated leather, the after-treatment in both cases resulted in an increase in the extractable chrome and a reduction in the total chrome respectively. The presence of the reducing chemical agent lowered the chrome fixation (e.g. pH shift).

The results are presented in *Panel 8*.

The after-treatment was also carried out on thick upper leather, which was subsequently split into three layers. Comparison of the layer-wise analysis with the analysis of the non-split leather indicates that, in general, the grain split has the highest Cr(VI) content whereas the middle split has the lowest. The results also indicate the major effect of both reducing agents, and that the ascorbic acid had the strongest influence. The Cr(VI) content of all splits of the treated leathers were under the 3 mg/kg detection limit. The exception was the grain split treated with product X as shown in *Panel 9*.

The leathers were also subjected to an extended UV irradiation (120 hrs, 150W, 50°C, using a specially made apparatus with four UV lamps). This favoured a strong generation of Cr(VI) in

Panel 9: Chrome (VI) distribution in leather cross-section: after treatment with Product X



an attempt to overcome the reduction effect of ascorbic acid and Product X used in the post-treatment. However, the research conditions were insufficient to overcome the effects of the after-treatment, as the results in *Panel 10* support:

Panel 10: Influence of post-treatment after extended UV radiation

Sample	Chrome VI (mg/kg TS)	
	Original 2 weeks after production	After 120 hours radiation 10 weeks after production
Crust upper leather		
original	7.05	8.95
with ascorbic acid	(0.92)	(1.95)
with product x	(1.49)	(2.75)
Crust lining leather		
original	2.98	15.04
with ascorbic acid	<0.75	<0.75
with product x	<0.75	(2.10)

Factors influencing the formation of Cr(VI) in leather manufacture

The results of the investigations performed at LGR may be summarised as follows:

- Constituents in the hide structure had no definitely recognisable influence on the formation of Cr(VI). This is supported by the fact that pure (denatured) collagen that was chrome tanned did not give rise to Cr(VI) formation.
- Some modern fatliquors stabilised to oxidation were unable to inhibit the formation of Cr(VI) on exposure of the leather to UV radiation.
- Reducing agents used in the investigation were effective whether applied in the float as after-treatment or as an after-spray; they remained effective after heat treatment. Under the research conditions the reducing potential was not exhausted by considerably extended heat/UV radiation exposure.
- Choice of finishing components is important. Finishing with certain alkaline adhesion binders can promote the formation of Cr(VI) on heat ageing, and particularly with UV exposure.
- There is a linear relationship between total and soluble chrome content but no significant relationship between soluble chrome and Cr(VI) content.
- Regarding chrome distribution in splits:
 - a) There is a distinct difference in the chrome distribution. The total chrome content as expected was higher in the outer splits and less in the middle. However, the extractable total chrome was less in the outer splits compared to that present in the middle split.
 - b) The Cr(VI) content was greater in the outer splits regardless of the leather being split before or after heat and UV exposure. ☺

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