



Relationships in the formation of hexavalent chrome [Cr(VI)] (Part 2)

Ines Anderie and Kerstin Schulte

Test and Research Institute Pirmasens, Germany

Leder Institute Reutlingen (LGR) has 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 limits of the analytical procedure above 3 mg/kg for leathers in daily use.

Despite extensive research, 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 unbound (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 the regulations. In addition, feasible procedures are needed to permanently remove any Cr(VI) content from the leather and intermediates^(7, 8).

Investigations relating to leather production were carried out at The Leder Institute Reutlingen. Entitled "Relationship of the formation of hexavalent chrome (VI)" (Part 1), these were published in World Leather June/July 2011, and a summary is given in Panel 1.

Investigations regarding the manufacture of leather articles - presented in this paper - were carried out by the Test & Research Institute Pirmasens (PFI), where the potential influence of adhesives and heat on the formation of Chrome (VI) in leather and shoes were investigated.

Chrome (VI) generation within leather according to adhesives and heat treatment

South German bovine hides were made into shoe upper and lining leather and used in this investigation. Adhesives were applied in a thin layer to the inner-side of the leathers, and then incubated for 21 days at room temperature in the dark. After this incubation the leathers were divided into two parts:

- One part of the leather was treated in a heat-setting procedure at 120°C for 15 minutes.
- The second part was used as a control, and not subjected to the heat setting process.

Subsequently Chrome (VI) was determined for both of these parts.

Three different water-based adhesives with alkaline pH-values were chosen for this incubation as alkaline adhesives may promote Chrome (VI) formation. The adhesives used were:

- Latex adhesive (pH-value 8.0-9.0)
- Synthetic latex adhesive (pH-value 8.0-9.0)
- PU-dispersion adhesive (pH-value 7.5)

All of these leathers originally had pH-values between 3.6 – 4.0, and this treatment with adhesives resulted in a small increase of pH-values of about 0.2 units. However, short-term localised increasing pH-values on the treated surface area cannot

be ruled out.

Upper leathers and lining leathers (UL and LL respectively) which were produced with different offers of chrome during tanning were covered on their inner-side with adhesives. The formation of Chrome (VI) was followed after three days and 21 days, and the results are given in Panel 2.

The upper leathers that were tested revealed only a minor potential to form Chrome (VI).

In contrast, high concentrations of Chrome (VI) could be measured in the lining leathers where their content of Chrome (VI) increased from day 3 until day 21. Moreover, subsequent heat-setting led to further increasing Chrome (VI) concentrations.

The maximum increase of Chrome (VI) formation of these leathers was observed using adhesives based on PU-dispersion. The lowest increase in Chrome (VI) formation was achieved after treatment with latex adhesive.

Chrome (VI) formation during production of shoes

Two representative upper and lining leathers with different levels of chrome content were chosen for the production of shoes. The chrome offer for tanning is given in Panel 3.

With reference to Panel 2, latex adhesive (which had the smallest influence on Chrome (VI) formation) and PU-dispersion adhesive (which supported Chrome (VI) formation) were used for adhesion in shoe production. Shoes and semi-finished shoes were manufactured out of four pieces of upper leather (UL) and four pieces of lining leather (LL) - front part, heel part, inner-side part

**Panel 1: 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.

and outer-side part. Examples of these are shown in *Panel 4*.

Chrome (VI) measurements started directly after shoe construction was complete. All upper and lining leathers from each shoe and the semi-finished shoes were analysed for Chrome (VI) formation. The results are shown in *Panel 5*.

Remarkably, on shoes and semi-finished shoes that were produced using PU-dispersion adhesive no Chrome (VI) developed in the upper leathers. In contrast, in shoes and semi-finished shoes that were fabricated using latex adhesive, slightly increased Chrome (VI) concentration were found in the upper leathers of the heel part.

Moreover, the Chrome (VI) concentration of the lining leathers increased during shoe production independently of the adhesive used. No significant difference in Chrome (VI) formation between semi-finished shoes and the final shoe could be recognised.

Selected upper and lining leathers out of the front part of the shoes were analysed again for their Chrome (VI) concentration after a period of 90 days. These findings are set down in *Panel 6*.

During this long term incubation of shoes, Chrome (VI) of both the upper leathers and the lining produced from the maximum offer of chrome (UL3 and LL3 – both at 2.5% chrome offers respectively) increased when compared to upper and lining leather with the lower offers of chrome (UL2 and LL2 – both at 1.5% chrome offers).

In general, the lining leathers were more predisposed to Chrome (VI) formation. No major influence of either the latex adhesive or PU-dispersion adhesive was detected on Chrome (VI) formation.

TEST METHODS USED IN THE INVESTIGATION:

The determination of Chrome (VI) was according to EN ISO 17075. This detection limit of analytical procedures for Chrome (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 (ie. not detectable) Cr(VI)/kg leather. For research purposes, these in-house detection limits were used to establish tendencies, illustrated in graphs and tables.

Panel 2: Chrome (VI) concentration in upper and lining leathers after adhesive and heat treatment

	Chrome(VI) [mg/kg]					
	UL	UL	UL	LL	LL	LL
Adhesives	0.5 %	1.5 %	2.5 %	0.5 %	1.5 %	2.5 %
Latex 3 day	n.d.	n.d.	1.8	n.d.	n.d.	0.9
Latex 21 day	n.d.	n.d.	n.d.	n.d.	2.9	1.6
Latex 21 day with heat	n.d.	n.d.	0.9	n.d.	4.3	3.1
Synthetic Latex 3 day	n.d.	n.d.	n.d.	n.d.	1.8	n.d.
Synthetic Latex 21 day	n.d.	n.d.	n.d.	n.d.	3.7	n.d.
Synthetic Latex 21 day with heat	1.9	n.d.	n.d.	2.6	7.0	3.3
PU-Dispersion 3 day	n.d.	n.d.	n.d.	n.d.	n.d.	4.1
PU-Dispersion 21 day	1.0	n.d.	n.d.	n.d.	n.d.	6.1
PU-Dispersion 21 day with heat	0.9	n.d.	3.5	1.4	10	8.8

Panel 3: Total chrome offer of selected leather for shoe production

Leather	Chrome used for tanning
UL 2	1.5 %
UL 3	2.5%
LL 2	1.5 %
LL 3	2.5 %

Treatment with reducing agents for the elimination of Chrome (VI)

A post treatment with reducing agents was performed by spray application. This was applied to both lining and upper leathers with Chrome (VI) concentrations above 3.0mg/kg.

Ascorbic acid (3%) and Hexagon (*Hexagon solutions®*, *Erren Recondition*, Netherlands) were used as reducing agents.



Panel 4: Example of shoes made out of different upper and lining leathers and different adhesive. 'B' shows examples semi-finished shoes.



One day after the treatment, the leathers were coated with the latex adhesive and PU-dispersion adhesive, and then incubated for 21 days in the dark at room temperature. The findings are presented as *Panel 7*.

This shows that after 21 days of incubation:

- In the non-treated lining leathers, the Chrome (VI) content increased to 9.2 mg/kg and 6.6 mg/kg.
- In the non-treated upper leathers, the Chrome (VI) remained unchanged.
- Treatment with ascorbic acid and Hexagon eliminated Chrome (VI) for all leathers.
- The adhesives also reduced Chrome (VI) concentration in all tested leathers.
- No significant influence of adhesive on the reducing properties of the reducing agents used could be observed.

One lining leather (*LL1*) and one upper leather (*UL3*) were chosen for activation by heat, and the findings are presented in *Panel 8*.

This shows that:

- Heat activation did not influence the reducing properties of ascorbic acid and Hexagon.
- The Chrome (VI) concentration of the leathers treated with reducing agents did not increase after heating when compared to the control leathers that were not subjected to reducing treatment.
- Heat activation of the lining leather that was pre-treated with reducing agents and adhesives resulted in an increase of Chrome (VI) formation.
- The upper leather remained unchanged by heat activation.
- In general, the influence of the reducing agents to eliminate Chrome (VI) in leathers was not affected, or only slightly influenced, by adhesives and heat.

The shoes that were incubated for 90 days (*re: Panel 6*) were treated with reducing agents. Two different shoes were selected, one produced with latex adhesive and one produced with PU-dispersion adhesive. Hexagon was applied to the lining leathers, and two days after this reducing treatment Chrome (VI) was measured. The findings are presented as *Panel 9*.

This shows that Chrome (VI) could be eliminated by post-treatment of the shoes with reducing agents.

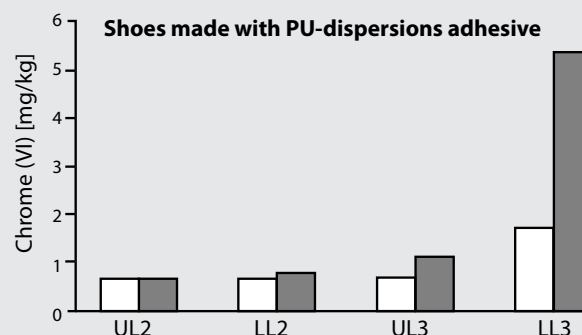
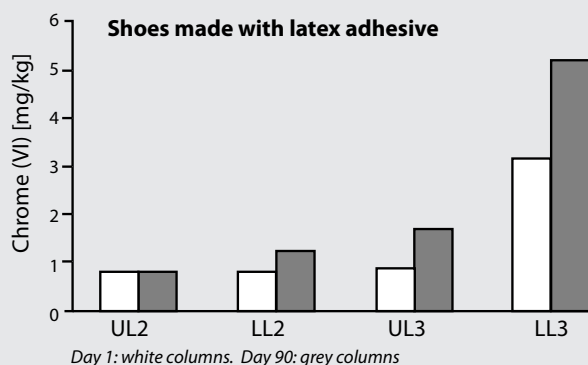
Panel 5: Chrome (VI) measurements on shoes and semi-finished shoes. Adhesives used: latex adhesive or PU-dispersion adhesive

		Chrome(VI) [mg/kg]							
Material		Outer side		Inner side		Front		Heel	
		UL	LL	UL	LL	UL	LL	UL	LL
Latex adhesive									
Shoe	OL 2 / LL 2	n.d.	12	n.d.	2.0	n.d.	n.d.	n.d.	1.2
Semi-finished	OL 2 / LL 2	n.d.	8.8	n.d.	1.2	n.d.	n.d.	n.d.	n.d.
Shoe	OL 3 / LL 3	n.d.	n.d.	1.1	n.d.	0.8	3.1	2.6	n.d.
Semi-finished	OL 3 / LL 3	0.8	n.d.	n.d.	n.d.	n.n	2.3	2.0	n.d.
PU-Dispersion adhesive									
Shoe	OL 2 / LL 2	n.d.	n.d.	n.d.	1.9	n.d.	n.d.	n.d.	n.d.
Semi-finished	OL 2 / LL 2	n.d.	1.3	n.d.	0.9	n.d.	n.d.	n.d.	3.5
Shoe	OL 3 / LL 3	n.d.	n.d.	n.d.	n.d.	n.d.	1.7	n.d.	3.1
Semi-finished	OL 3 / LL 3	n.d.	n.d.	n.d.	n.d.	0.8	n.d.	n.d.	2.4

(UL = upper leather, LL = Lining leather)

As reducing agents these products should eliminate Chrome (VI) formation, leaving only Chrome (III) present in the leathers.

Panel 6: Chrome VI measurement of upper and lining leather from shoes 90 days after production.





Panel 7: Chrome(VI) concentration within Chrome (VI) containing leathers after spray application of reducing agents and treatment with adhesives.

Conditions	Chrome(VI) [mg/kg]				
	LL 1	LL 2	UL 3	UL 4	UL 5
Day 1: no adhesive	7.7	3.6	5.4	3.3	4.9
Day 21: no adhesive	9.2	6.6	5.1	3.4	4.9
Day 21: Ascorbic acid/ no adhesive	1.1	n.d.	1.6	2.1	2.5
Day 21: PU-Dispersion adhesive only	3.1	2.2	2.5	3.2	2.6
Day 21: Ascorbic acid with PU-Dispersion adhesive	n.d.	n.d.	1.9	2.1	2.7
Day 21: Hexagon with PU-Dispersion adhesive	0.9	1.4	2.2	2.5	2.5
Day 21: Latex adhesive only	2.7	1.5	1.7	1.5	2.2
Day 21: Ascorbic acid with Latex adhesive	n.d.	n.d.	1.6	1.3	2.2
Day 21: Hexagon with Latex adhesive	n.d.	n.d.	1.5	1.9	2.4

Panel 8: Chrome (VI) concentration in Chrome (VI) containing leathers after spray application of reducing reagents and following treatment with adhesives and heat

Conditions	Chrome(VI) [mg/kg]			
	LL1		UL3	
	no heat	heat	no heat	heat
No adhesive	9.2	14	3.1	2.4
Ascorbic acid without adhesive	1.1	n.d.	1.6	1.6
Hexagon without adhesive	n.d.	1.9	2.4	1.8
PU-Dispersion adhesive only	3.1	1.3	2.5	1.8
Ascorbic acid with PU-Dispersion adhesive	n.d.	5.4	1.9	1.3
Hexagon with PU-Dispersion adhesive	0.9	2.1	2.2	1.3
Latex adhesive only	2.7	3.6	1.7	1.5
Ascorbic acid with Latex adhesive	n.d.	n.d.	1.6	1.3
Hexagon with Latex adhesive	n.d.	1.5	1.5	1.5

Findings from the investigation

Adhesives and heat are two important factors during the production process of shoes, and the objective of this investigation was to study the influence of their influence on Chrome(VI) formation in leathers.

In addition, the influence of adhesives and heat on the properties of reducing agents was studied. The findings from these investigations are summarised:

- Chrome (VI) studies during shoe production process lead to the conclusion that lining leathers tend to significant increase in Chrome (VI) formation. In contrast upper leathers mostly withstand the production processes, with a minor potential to form Chrome (VI).
- No clear statement can be given for the influence of adhesives in Chrome (VI) formation. In general, all essential workflows in shoe production, with heat, pressure and adhesive treatment may increase Chrome (VI) values in upper and lining leathers.
- The long term incubation testing lead to the result that leathers which were tanned with higher Chrome amount

Panel 9: Chrome (VI) concentration of the lining leather from shoes after spray application of reducing reagent

Shoe made with	Chrome(VI) [mg/kg]		
	day 1	day 90	day 92 +Hexagon
PU-Dispersions adhesive	1.9	5.9	1.1
Latex adhesive	n.d.	4.8	n.d.

formed more Chrome (VI) than the leathers which were tanned with lower Chrome amount.

- By comparing the findings set down in *Panel 2* (where leathers with low initial Chrome (VI) contents were used for testing) with *Panel 8* (with the Chrome (VI) containing leathers), it appears that:
- the formation of Chrome (VI) was promoted by heat and/or adhesives in leathers with low initial Chrome (VI) values.
- the Chrome (VI) in Chrome (VI) containing leathers, with high initial Chrome (VI) contents seemed to be reduced by heat and adhesive treatment.
- Use of reducing agents for post-treatment of shoes consistently leads to lower Chrome (VI) contents of leathers. The reducing potential withstood treatment with heat and adhesives and the Chrome (VI) content of leathers and shoes could be decreased. ☺

Acknowledgements

Research Council of German Leather Industry – “Forschungsgemeinschaft Leder (FGL) e.V.”

German Federal Ministry of Economy and Technology for funding of the project (No. 15845 N) within the program of Industrial Cooperative Research (IGF).

All the colleagues at PFI involved in the project.

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