

Investigations on a possible formation and avoidance of chromate in leather 1999

Dr. Christiane Hauber and Dr. Heinz-Peter Germann, Lederinstitut Gerberschule Reutlingen, Germany

Chrome tannage is the most important tanning method representing over 80% of leather production. It is very versatile and no change is expected in the foreseeable future.

Chromate[Cr(VI)] has sometimes been detected in chrome tanned leathers. This is unexpected because in the presence of a high proportion of organic matter and low pH, chrome(VI) is unstable, and chrome(III) is produced by reduction.

Various possibilities for the presence of Cr(VI) have been cited:

Neutralisation of the wet-blue, as during this treatment the acid present is neutralised and the pH raised.

Any dyeing pre-treatment in order to level the dyeing and improve penetration. Ammonia is sometimes used, often in an overnight float to promote through dyeing.

Drying and intermediate drying might provide conditions for the formation of Cr(VI). It is also thought possible that heat and light can oxidise Cr(III) to Cr(VI).

The influence of ratty acids in fatliquors cannot be ignored.

Details of the investigation

In a series of investigations clothing, upholstery and water resistant shoe upper leathers were produced to cover the main leather types. The pelt was chrome tanned to the wet-blue stage, neutralised in various ways and taken to the crust. After additions to give good dye penetration, the leathers were dyed. Redox potentials were determined at the individual process stages in order to assess the oxidative or reductive properties of the floats. In addition, 5 and 10 mg/l chromate was added and the influence of the reduction measured according to DIN 38405.

The effects of retannage and fatliquoring were also investigated. The Cr(VI) content of the undyed/dyed leathers in their intermediate states were analysed photometrically according to DIN 53314 using the reaction between Cr(VI) and 1.5 diphenyl carbazide.

The leather was analysed in:

- the dried aired-off State.
- after heating at 80°C for 24 hours in a drying chamber.
- after subjection to UV radiation for 48 hours in a Xenotest apparatus.

It should be noted that the conditions created by treatments (b) and © are extreme and unlikely to be met in normal use.

The influence of neutralising

The redox and chromate reduction potential in the neutralisation of wet-blue for upholstery crust, clothing and water resistant shoe-upper were assessed.

The wet-blue was neutralised conventionally, using sodium formate and sodium bicarbonate and compared with a reducing auxiliary. The reducing potential was also checked by the addition of 5 and 10 mg/1 Cr(VI) to the float.

No relationship could be established between the chromate reduction property of the float and the Cr(VI) content of the leather produced. The Cr(VI) content of the various crust leathers were below 3mg/kg, the detection limit based on dry substance.

However, when the results involving heating at 80°C for 24 hours are considered, it can be seen that in isolated cases of the Standard neutralisation Cr(VI) is detectable. This is shown in Table 1.

The influence of wetting back agents before dyeing crust leathers

The reduction tendency of the bath before dyeing was investigated on different leathers with various wetting back agents. The results are given of dyeings on crust upholstery leathers with:

- standard neutralisation using sodium formate and sodium bicarbonate
- the addition of reducing auxiliary agents to the Standard neutralisation.

It was found that the Cr(VI) content of all the air dried leathers was below the detection limit. However, after heating at 80°C for 24 hours, the ammonia or sodium bicarbonate treated samples contained chromate as shown in Table 2.

Table 1:

Table 1 The Potential of Cr(VI)-Formation in Crust Leather as depending on Neutralisation

Leather Type	Heat Treatment	Reduct. Neutralisat. mg Cr(VI)/kg DS	Standard-Neutralisat. mg Cr(VI)/kg DS
Garment			
Wet Blue	-	n.d.	n.d.
Crust	-	n.d.	n.d.
	60°C	n.d.	n.d.
	80°C	n.d.	4,3
Waterproof			
Crust	-	n.d.	n.d.
	80°C	n.d.	n.d.
Upholstery			
Crust	-	n.d.	n.d.
	80°C	n.d.	7,0

n.d. = not detectable DS = dry sub

In further investigations a reducing auxiliary was used as a wetting back agent before dyeing, and in another experiment ammonia. The acidification for fixation was carried out at the end of the dyeing process with ascorbic acid instead of formic acid normally used. This was to ensure an especially high reducing ability of the acidification float. Despite the higher reducing properties of both the wetting back float and acidification, Cr(VI) formation could not be prevented in subsequent heating at 80°C for 24 hours.

The influence of vegetable retannage

Experiments with water resistant shoe upper leather showed that the crust and dyed leather even after extreme treatment showed no Cr(VI) content. The main difference from the upholstery and clothing recipes was the use of mimosa. Experiments were therefore carried out with different retannages. Wet blue leathers were neutralised conventionally with sodium formate/bicarbonate and retanned with either 10% tara, 10% mimosa, 10% synthetic tanning agent or a chrome containing tanning material. A blank test was made without retannage. All were given 8% fatliquor containing natural and synthetic components and finished conventionally into crust. The findings are presented in Table 3.

As a result of these findings further retannages were applied at 3% offers of mimosa, tara, chestnut, quebracho (ordinary and sulfited). Standard neutralisation and neutralisation with a reducing auxiliary were used and the findings are shown in Table 4.

For many leather types it is not possible to add large amounts of vegetable retan therefore lower offers were made to determine the level at which a reduction in chromate production was noticeable.

The results of offers of tara and mimosa when neutralised and fatliquored with 8.0% fatliquor containing natural and synthetic components are given in Table 5 and Table 6.

It is clear that after extreme conditions -heat and UV exposure - the mimosa did not prevent chromate formation. Tara, however, was better and all results were successful in achieving the avoidance of Cr(VI) formation.

The „blank“ showed that although under normal drying conditions Cr(VI) was not detected, under extreme exposure conditions relatively high Cr(VI) values resulted.

Table 2 to 4:

Table 2 The Potential of Cr(VI)-Formation in dyed Crust Leather as depending on Wetting-back agents

Wett-back Agent	Heat Treatment	Reduct. Neutralisat. mg Cr(VI)/kg DS	Standard-Neutralisat. mg Cr(VI)/kg DS
Reduct Auxiliary	- 80°C	n.d. n.d.	n.d. n.d.
Cation. Fatliquor	- 80°C	n.d. n.d.	n.d. 3,6
Ammonia	- 80°C	n.d. 19,5	n.d. 14,4
Sodium-bicarbonate	- 80°C	n.d. 37,1	n.d. 40,3

n.d. = not detectable DS = dry sub

Table 3 The Potential of Cr(VI)-Formation in Crust Leather as depending on Retannage

Retannage	Heat Treatment	mg Cr(VI)/kg DS
Tara (10%)	- 80°C	n.d. n.d.
Mimosa (10%)	- 80°C	n.d. n.d.
Sytan (10%)	- 80°C	n.d. 19,9
Chrome (0,75% Cr₂O₃)	- 80°C	n.d. 26,5
Water (Reference)	- 80°C	n.d. 39,9

n.d. = not detectable DS = dry sub

Table 4 Avoidance of Cr(VI)-Formation by Vegetable Retannage

Wett-back Agent	Heat Treatment	Reduct. Neutralisat. mg Cr(VI)/kg DS	Standard-Neutralisat. mg Cr(VI)/kg DS
3% Mimosa	- 80°C	n.d. n.d.	n.d. n.d.
3% Tara	- 80°C	n.d. n.d.	n.d. n.d.
3% Chestnut	- 80°C	n.d. n.d.	n.d. n.d.
3% Quebr. ord.	- 80°C	n.d. n.d.	n.d. n.d.
3% Quebr. sulf.	- 80°C	n.d. n.d.	n.d. n.d.

n.d. = not detectable DS = dry sub

Table 5 to 6:

Percentage used	Retannage	Sample	mg Cr(VI)/kg DS
4%	Tara	air-dried	n.d.
		80°C	n.d.
		UV	n.d.
2%	Tara	air-dried	n.d.
		80°C	n.d.
1%	Tara	air-dried	n.d.
		80°C	n.d.
0,5%	Tara	air-dried	n.d.
		80°C	n.d.
0,25%	Tara	air-dried	n.d.
		80°C	3,3
		UV	n.d.
-	(without)	air-dried	n.d.
		80°C	69,2
		UV	27,5

n.d. = not detectable DS = dry sub

Percentage used	Retannage	Sample	mg Cr(VI)/kg DS
4%	Mimosa	air-dried	n.d.
		80°C	4,5
		UV	3,0
2%	Mimosa	air-dried	n.d.
		80°C	3,2
1%	Mimosa	air-dried	n.d.
		80°C	5,7
0,5%	Mimosa	air-dried	n.d.
		80°C	6,9
0,25%	Mimosa	air-dried	n.d.
		80°C	4,5
		UV	3,5

n.d. = not detectable DS = dry sub

The influence of fatliquors

From the results presented, and other investigations, there was evidence of a linkage between Cr(VI) formation, neutralisation and wetting back agents. In addition, with the same retannage differences could occur with various fatliquors in the amounts of chromate found. It was thought that the influence of the fatliquoring could be due to the effects of unsaturated fats on Cr(III) oxidation. It was considered that raw fat materials of high iodine value (more unsaturation) could play a role in Cr(VI) formation.

Experiments were therefore undertaken, after a chrome retannage and normal neutralisation with sodium formate/bicarbonate to a maximum pH of 5,5. Fatliquors were offered at 10% including fish oils of different iodine value. These findings are represented as Table 7.

No differences were found between sulfited fish oils with different iodine values when air dried or dried at 80°C.

However, with lower iodine values, the chromate contents of leathers after UV exposure were distinctly lower.

Table 7 and Table 8:

Table 7 The Influence of Fatliquoring

Fatliquor	air-dried	mg Cr(VI)/kg DS 80°C	UV
0% Fatliquor	n.d.	n.d.	n.d.
10% Fish oil sulfited (IV 150-160)	n.d.	40,0	32,4
10% Fish oil sulfited (IV 110-130)	n.d.	40,1	14,4
10% Synthetic Fatliquor	n.d.	n.d.	n.d.
10% Fish oil sulfited (IV 110-130)/ Alkyl sulphon. ester	n.d.	29,2	12,6

n.d. = not detectable DS = dry sub

Table 8 The Influence of Fatliquoring

Fatliquor	air-dried	mg Cr(VI)/kg DS 80°C	UV
Synthetic Fatliquor (free of oleic acid)	n.d.	n.d.	n.d.
Synthetic Fatliquor (contain oleic acid)	n.d.	20,7	9,8
Fish oil sulfited	n.d.	50,4	17,2
Fish oil sulfited Alkyl sulfonate ester	n.d.	47,4	13,1
Fish oil sulfonated	n.d.	16,2	20,3
Triolein sulfonated	n.d.	43,2	43,4
Alkyl sulfonate ester + White oil emulsion	n.d.	n.d.	6,2

n.d. = not detectable DS = dry sub

The effect of oleic acid and other variables

An overview of the fatliquor types used in this investigation is presented in Table 8.

This shows that as well as the degree of unsaturation, other fatty compounds - in particular oleic acid - affect the formation of Cr(VI). Oleic acid contains only a single double bond but can affect the oxidation of Cr(III) to Cr(VI). The analytical values show that no air-dried leathers had detectable chromate. After treating the synthetic fatliquor (without unsaturated components) was advantageous but also that in the presence of oleic acid chromate formation was a possibility.

It also shows that sulfonated and sulfited fish oils increase the tendency to Cr(VI) formation under the extreme conditions of heat and UV exposure.

The use of some lecithin-based fatliquors also appears undesirable, being used in the fatliquoring of clothing leathers.

The effects of retanning agents and fatliquors

The effects of polymer and mimosa retannages with fatliquors

It has been shown when using certain retanning materials and fatliquors there is no chromate formation even after extreme conditioning.

In a further series of experiments, the combination of specific fatliquors and retannages was examined. The results of combinations of fatliquors with a polymer or mimosa retannage is given in Table 9.

It can be seen that:

- in the Variation without fatliquor, the mimosa retannage was inferior to the polymer retannage.
- in the combination with fatliquor e.g. sulfited fish oil, the combinations with mimosa generally led to lower Cr(VI) values.

The effects of tara with different fatliquor combinations

Of the vegetable retannages, tara has particularly good effect in avoiding the formation of chromate. It was therefore used in combination with the fatliquor types used to assess the effects of oleic acid and other variables, (finding given as Table 8) to determine the amount of tara required to suppress chromate formation.

The wet blue were therefore neutralised in a similar manner, then retanned with varying offers of tara, washed and then fatliquored using a 10% offer. The findings are presented in Table 10.

It can be seen that:

- The only air dried leather showing a trace of Cr(VI) was produced using an oleic acid containing synthetic fatliquor without tara.
- That low levels of tara was unable to prevent the formation of chromate when using sulfited or sulfonated fish oils alone under extreme conditions of heat and UV exposure.
- In the case of tara at 2.0% offer and sulfited fish oil, traces of chromate were only detected after UV exposure.
- In all other cases, the tara retannage provided avoidance of all chromate formation.

Table 9 and 10:

Table 9 The Influence of different Combinations of Fatliquor and Retannage

Fatliquor	mg Cr(VI)/kg DS		
	air-dried	80°C	UV
0% Fatliquor/ Polymer	n.d.	n.d.	n.d.
0% Fatliquor/ Mimosa	n.d.	4,8	5,3
14% Fish oil sulfited/ Polymer	n.d.	35,6	18,2
14% Fish oil sulfited/ Polymer	n.d.	3,2	4,6
14% Synthet. sulfonated/ Polymer	n.d.	5,5	6,2
14% Synthet. sulfonated/ Mimosa	n.d.	n.d.	3,5

n.d. = not detectable DS = dry sub

Table 10 The Influence of Tara-Retannage on Cr(VI)-Formation for different Fatliquors

Fatliquor/Retannage	Sample	mg Cr(VI)/kg DS			
		0% Tara	0,25% Tara	0,5% Tara	2% Tara
Synthet. Fatliquor I (olein-contain)	air-dried	3,2	n.d.		
	80°C	65,0	n.d.		
	UV	31,8	4,0	n.d.	
Synthet. Fatliquor II (olein-free)	air-dried	n.d.	n.d.		
	80°C	n.d.	n.d.		
	UV	13,1	4,3	n.d.	
Fish oil sulfited	air-dried	n.d.	n.d.		
	80°C	47,1	36,4	8,4	n.d.
	UV	70,1	38,9	9,1	4,1
Fish oil sulfited Alkyl sulphon. ester	air-dried	n.d.	n.d.		
	80°C	6,6	3,3	n.d.	
	UV	51,7	34,9	5,9	n.d.
Fish oil sulfonated	air-dried	n.d.	n.d.		
	80°C	39,3	29,9	19,5	6,9
	UV	63,1	39,4	8,4	4,7
Triolein sulfonated	air-dried	n.d.	n.d.		
	80°C	5,2	3,5	n.d.	
	UV	49,5	23,7	n.d.	
(without)	air-dried	n.d.	n.d.		
	80°C	n.d.	n.d.		
	UV	5,6	n.d.		

n.d. = not detectable DS = dry sub

The influence of different types of tara

Different types of tara were investigated in the production of automobile upholstery leather being 71% and 50% tanning extract, 50% tan content liquid extract and a further extract with 61% tan

content. In these investigations a limited amount of conventional fatliquor was used during neutralisation and similarly in the retanning. The findings are presented in Table 11.

It can be seen that:

- the wet blue showed a chromate after exposure to UV.
- the leather after neutralisation, retanning without tara and fatliquoring had a noticeable chromate content after heat and UV exposure.
- all of the 4 tara extract treated samples showed no detectable chromate.

The influence of storage

Prevailing wisdom suggests that storage could increase chromate content. Some leathers - dothing, furniture, and shoe upper leathers - were stored for two months and reanalysed for chromate.

It was found that whilst some samples decreased, others increased compared with the original results.

However, where vegetable retanning agents and fatliquors were used that showed no formation of Cr(VI) in the fresh State, no presence was detected after storage.

These observations could account for the variability of analytical results of different workers that have been interpreted as inadequacies of analytical methods up to now. The results indicate an ongoing interchange between chrome complexes and other components in the leather with the tannage.

The influence of mechanical processes

In buffing, for example, in the production of nubuck, there is at least a surface heating effect. This was investigated to see if there was an influence on chromate formation.

No chromate formation was detected in leathers which were chromate free before buffing. Where there was detectable chromate present, a slight increase was found, depending on the applied energy (rotation speed).

In vacuum drying there is a short heat application but no chromate formation occurs in leathers which are chromate free.

Table 11:

Table 11 The Influence of different Tara - Retanning Agents

Sample/Variant		air-dried	mg Cr(VI)/kg DS 80°C	UV
Wet Blue	- original	n.d	n.d.	3,7
	- neutralised	8,2	10,2	16,7
Retannage	- no Tara	n.d	20,1	23,8
	Tara: - Extract 71%	n.d	n.d.	n.d.
	- Tan. agent 50%	n.d	n.d.	n.d.
	- Liq. extract 50%	n.d	n.d.	n.d.
	- Extract 61%	n.d	n.d.	n.d.
Fatliquor (Crust)	- no Tara	9,2	32,4	33,7
	Tara: - Extract 71%	n.d	n.d.	n.d.
	- Tan. agent 50%	n.d	n.d.	n.d.
	- Liq. extract 50%	n.d	n.d.	n.d.
	- Extract 61%	n.d	n.d.	n.d.

n.d. = not detectable DS = dry sub

Summary of findings

- Measurement of redox potential of process liquors show no linkage to chromate formation.
- Measurement of chrome reduction properties of the individual process liquors showed no connection with the chromate content of the processed leather.
- The partial replacement of normal neutralisation materials by a reducing auxiliary, was found to reduce chromate formation.
- The use of a reducing auxiliary prior to dyeing is recommended. Stronger alkaline agents such as ammonia or sodium bicarbonate should be avoided.
- The type of fatliquoring agent has a profound influence on the possibilities of chromate formation.

The greatest effect is shown by:

- the dactical sulfonated and sulfited fish oils
- products with simple or multiple unsaturated free or esterified fatty acids.

Natural or synthetic fatliquoring agents which do not contain diese substances, do not lead to chromate formation.

- Synthetic and polymeric retanning materials are not conducive to the formation of Cr(VI). In critical leathers diese products do not prevent the formation of Cr(VI) on extreme heat and UV exposure. Vegetable retannage plays a significant part in avoiding chromate formation. In the research mimosa, quebracho, chestnut and tara showed a positive influence in leathers exposed to extremes of heat and UV exposure. Tara is particularly effective, where on some leathers even an addition of 0.25% produced suppression of chromate formation.

- Both reductions and increases in chromate content of the leather were found after 2 months storage. Where vegetable retanning agents and fatliquors were used that showed no formation of Cr(VI) in the fresh State, no presence was detected after storage.
- When leathers contain Cr(VI), buffing can give rise to an increase in Cr(VI). This does not occur in leathers which show no Cr(VI) before buffing.
- Vacuum drying has no influence on Cr(VI) formation.

References

1. Cory, N.J.: JALCA 92(1997), 119.
2. Gruppo Soci veneti AICC: Konferenzbericht (1998)
3. Nickolaus G.: XI International Congress on the Leather, Shoe Industries proceedings, Budapest (1998)
4. Püntener A.: JALCA 91 (1998), 126
5. Shi B.: XXIV IULTCS Congress proceedings, London 1997
6. World Leather 11 (1998) Nov, 5.
7. DIN 53314: Bestimmung des Chrom(VI)-Gehaltes in Ledern.
8. DIN 38405: Photometrische Bestimmung von Chrom(VI) mittels 1.5-Diphenyl-carbazid (D24)
9. DIN 38404: Physikalische und physikalisch-chemische Kenngrößen (Gruppe Q-Bestimmung der Redox-Spannung).

Selective extracts of this is not permitted without written permission of the publisher.

Publication:

C. Hauber, H.-P. Germann, Investigations on a possible formation and avoidance of chromate in leather 1999, World Leather 12, 10/1999, No. 6, p. 73 - 80

Kategorien:

[Alle-Seiten](#), [Gesamt](#), [abwasserbehandlung-gerberei](#), [Gerbung](#), [chrom-vi](#), [ledertechnik](#), [Lederherstellung](#), [Veröffentlichungen](#), [Sonderdrucke](#), [Umwelt](#), [english-content](#)

Quellenangabe:

[Quellenangabe zum Inhalt](#)

Zitierpflicht und Verwendung / kommerzielle Nutzung

Bei der Verwendung von Inhalten aus [Lederpedia.de](#) besteht eine Zitierpflicht gemäß Lizenz [CC Attribution-Share Alike 4.0 International](#). Informationen dazu finden Sie hier [Zitierpflicht bei Verwendung von Inhalten aus Lederpedia.de](#). Für die kommerzielle Nutzung von Inhalten aus [Lederpedia.de](#) muss zuvor eine schriftliche Zustimmung ([Anfrage via Kontaktformular](#)) zwingend erfolgen.

[www.Lederpedia.de](#) - Lederpedia - Lederwiki - Lederlexikon

Eine freie Enzyklopädie und Informationsseite über Leder, Ledertechnik, Lederbegriffe, Lederpflege, Lederreinigung, Lederverarbeitung, Lederherstellung und Ledertechnologie

From:
<https://www.lederpedia.de/> - Lederpedia - Lederwiki - Lederlexikon

Permanent link:
https://www.lederpedia.de/veroeffentlichungen/englisch/investigations_on_a_possible_formation_and_avoidance_of_chromate_in_leather_1999

Last update: 2019/05/02 18:18

