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Council for Leather Exports

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Study of the variation of chromium VI content inside the leather used in footwear

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The goal: to secure the supply chain

In the world

- More than 80% of the leather is tanned with Chromium
- The first use of leather : footwear

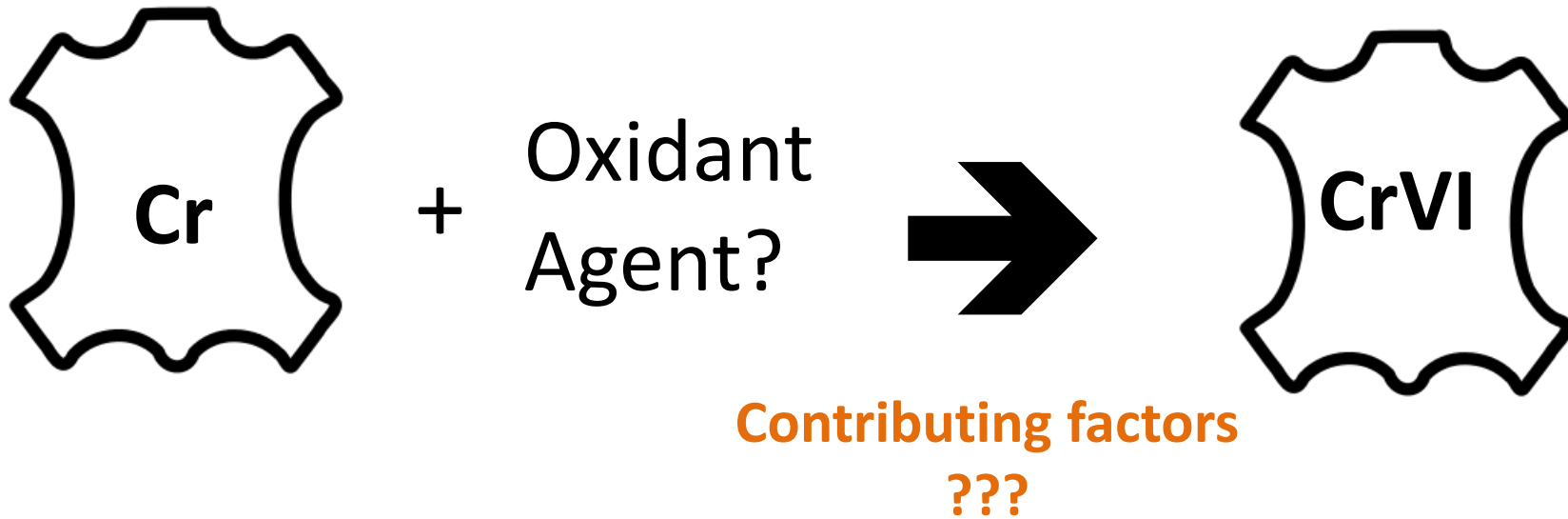
Only trivalent chromium (CrIII) is employed for tanning. However, if the process is not perfectly mastered, some hexavalent chromium (CrVI) may appear in leather.

Since May 2015, the European legislation has changed.

CrVI's content in leather must not exceed 3 ppm.
(Reach annex 17, §47)

To guarantee the absence of Cr VI in leather is
THE major subject for the footwear industry now.



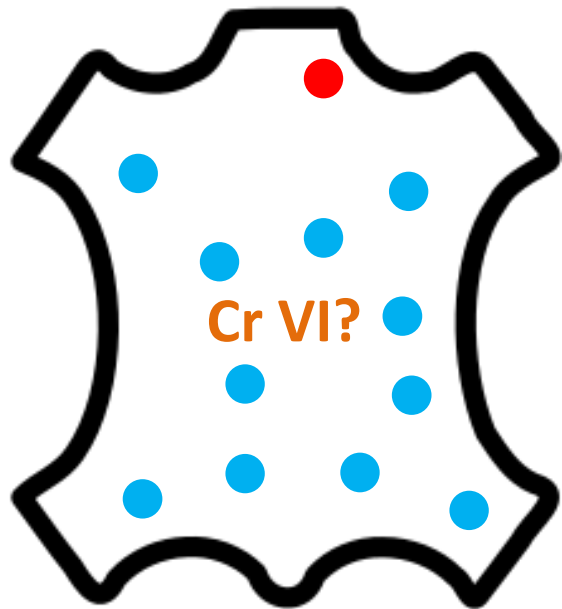


The target of our study:

- identify the critical parameters
- To define a good new ageing method

All the determinations of Cr VI have been performed according to: [pr EN ISO 17075-2 \(2015\)](#)

To validate the results of our laboratory, a inter-laboratory has been organised (IULTCS and CEN TC 289)



Mapping of Cr VI in full hides?

Several studies have been done.

The concentration of Cr VI has been observed as:

- Homogeneous in sheep skins
- Homogeneous in pig skins
- Not fully homogeneous in bovine hides on several selected samples

Systematic study on bovine:

Tests with a French-footwear manufacturer (ERAM), 83 leathers have been tested from an old stock

- 74 leathers were conform (less than 3ppm of Cr VI)
- 9 leathers were positive in the neck area and only 4 were positive in another area

Suggestion :

for Cr VI determination in leather, taking the sample in the neck area (in the most critical place) limits further risks of Non Compliance and Withdrawal from the market





Influence of the tanning process?

Four different bovine leathers have been produced:

- **Leather #1:** tanned and finished with all the best practices known nowadays (including the addition of reducing agent at the end of the process) to avoid CrVI generation
- **Leather #2:** treated with the same recipe as leather #1, except the fat liquors used, which are unsaturated.
- **Leather #3:** tanned without applying the best practices.
- **Leather #4:** treated the same way than leather #3, but with a vegetal retanning.

On these 4 leathers, we have studied the influence of :
Time, light, temperature, humidity, test preparation,...





Influence of the tanning process?

Time and temperature/light

After the process, the hides are cut in 2 pieces

- one stored in a warehouse
- one stored in a fridge (Darkness and at $4 \pm 2^{\circ}\text{C}$).

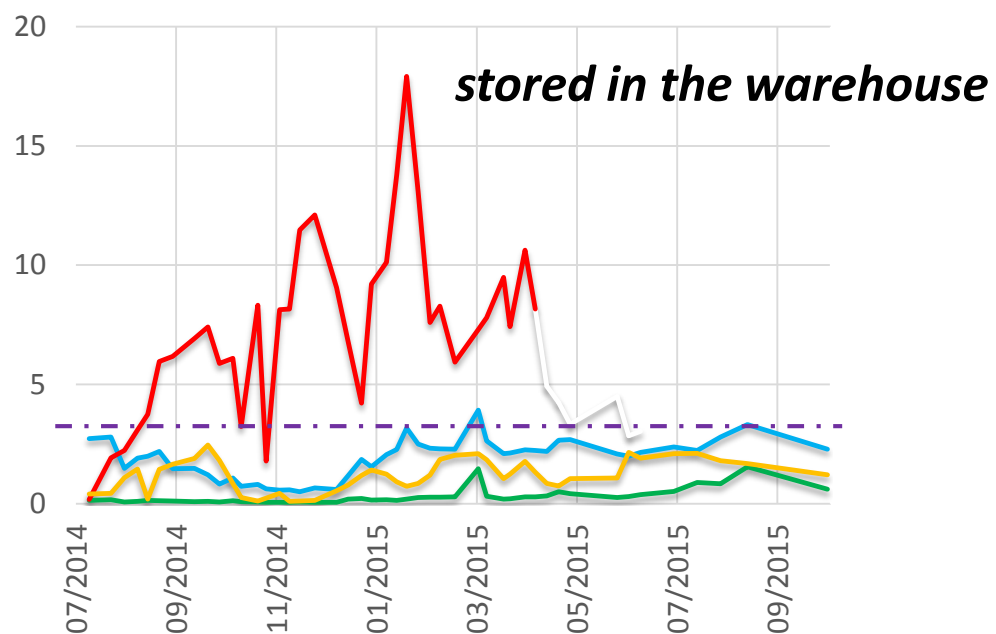
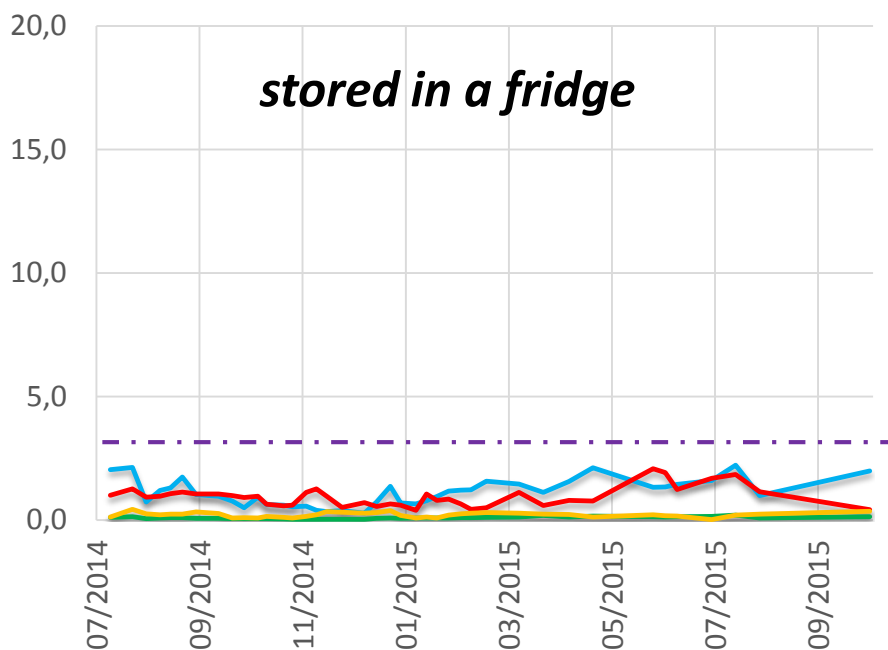
The Cr VI concentration in the 4 leathers have been analysed during several months.





Influence of the tanning process?

Time and temperature/light



The perfect knowledge on these specific leathers, allows us to decrease the L_Q





Influence of the tanning process?

Time and temperature/light

- **Leather 1:** tanned and finished with all the best practices known nowadays to avoid CrVI generation
- **Leather 2:** treated with the same recipe as leather 1, except the fat liquors used, which are unsaturated.
- **Leather 3:** tanned without applying the best practices.
- **Leather 4:** treated the same way than leather 3, but with a vegetal retanning.

After 16 months of ageing, the tendency is :

- No generation of chromium (VI) for the 4 leathers stored in a fridge (Darkness and at $4 \pm 2^{\circ}\text{C}$)
- No generation of chromium (VI) for the **leather#1** tanned and finished with all the best practices whatever the storage
- For **the leather#2** with fish oil, the chromium (VI) content is approached for the tolerance limit 3 ppm in the tannery conditions
- The **leather#3** tanned without applying the best practices is positive in the warehouse conditions
- The add of vegetable tannin blocks the chromium (VI) generation (**leather#4**)

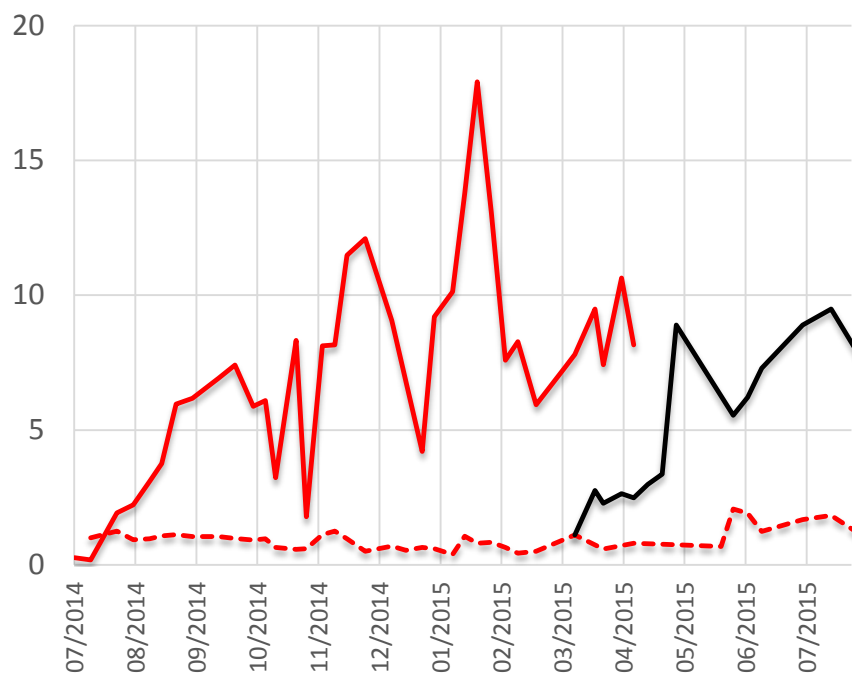




Influence of the tanning process?

Time and temperature/light

After 6 months in the fridge, a part of the leather 3 is stored in the warehouse.



The development of Cr VI on leather 3 is equivalent.

- Leather #3 in the warehouse
- Leather #3 in the fridge
- Leather #3 in the fridge 6 months then in the warehouse

Conclusion: Low temperatures and darkness stop temporarily the Cr VI appearance



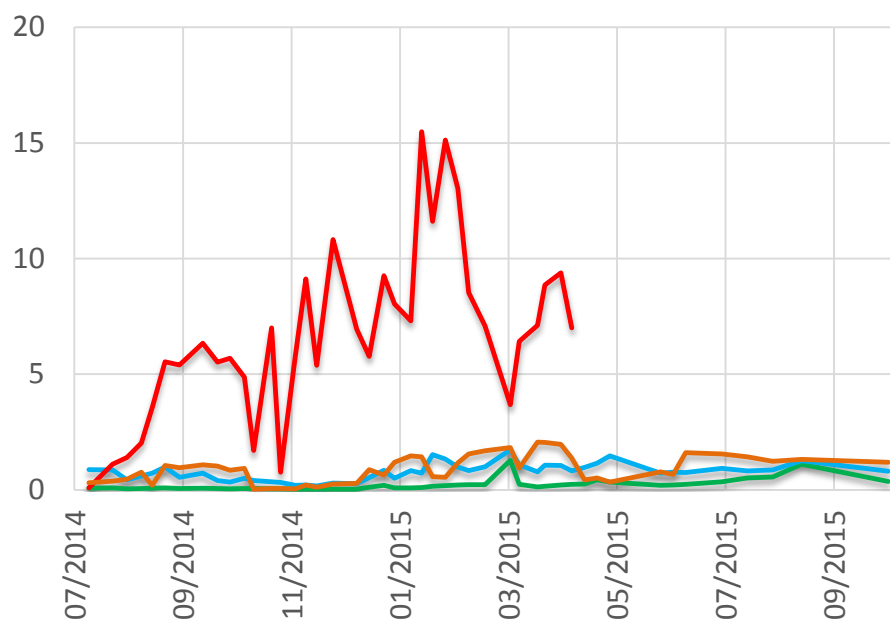


Influence of the tanning process?

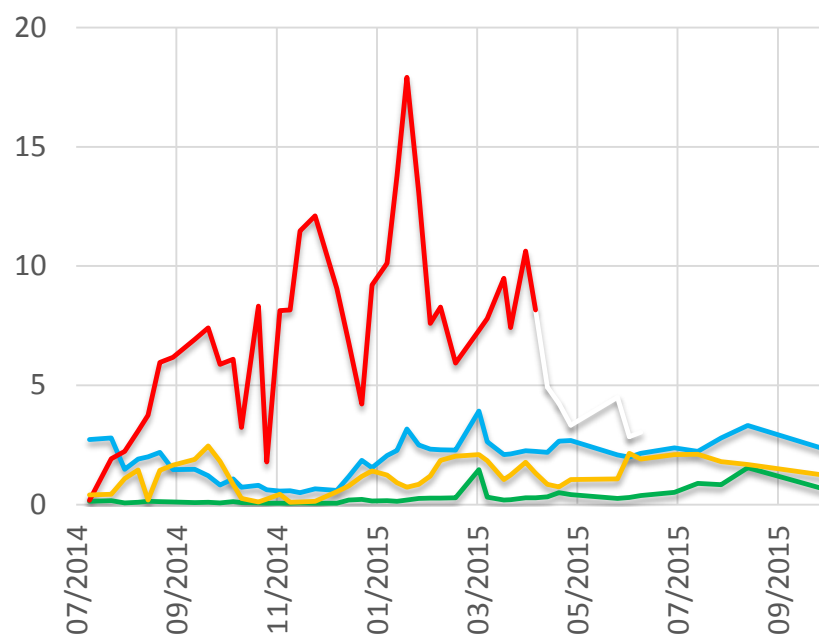
Influence of test preparation

Test are performed with 2 different preparations.

Cut samples



Grinded samples



Comparable results, the values for the grinded samples are slightly higher





Influence of the tanning process?

Influence of total and free chromium

tests with a French footwear manufacturer,
83 leathers have been tested from a old stock

Correlation?

- The 3 leathers most contaminated by chromium (VI) have a low concentration of free soluble chromium and total chromium.
- **No impact** between the highest concentrations of chromium free and the chromium (VI) generation

Sample	Chromium (VI) (mg/kg)	Free chromium (mg/kg)	Total chromium (g/kg)	Fat liquors (g)
1	< 3	110,1	21,8	0,48
2	3,2	59,0	26,4	0,46
3	< 3	28,1	22,7	0,34
4	3,0	133,2	25,9	0,39
5	13,6	63,6	26,8	0,38
6	3,9	297,3	8,5	0,68
7	12,1	26,5	28,0	0,44
8	16,7	30,8	28,2	0,46
9	5,3	43,6	20,3	0,86
10	< 3	230,4	23,1	0,29
11	3,1	20,6	17,4	0,37
12	3,8	30,5	20,9	0,32

No correlation between Cr VI – Cr total – Cr free





Influence of the tanning process?

Influence of ageing

Target : to define an ageing test method that reproduce in the laboratory what's happen in the warehouse after 1 year

Ageing conditions ^(*)		leather 1	leather 2	leather 3	leather 4
CTC warehouse	16 months	<3	<3	7,8	<3
80°C - less than 10 RH - no light	24 H	<3	<3	3.2	<3
80°C - 50 RH - no light	24 H	<3	<3	<3	<3
40°C - 20 RH - no light	24 H	<3	<3	<3	<3
40°C - 50 RH - no light	24 H	<3	<3	<3	<3
80°C - 20 RH - with light	24 H	<3	9,7	11,2	7,2
80°C - 50 RH - with light	24 H	<3	4,9	5,6	<3
40°C - 20 RH - with light	24 H	<3	3,7	5,6	<3
40°C - 50 RH - with light	24 H	<3	<3	4,6	<3



(*) Performed in a Xenotest



Influence of the tanning process?

Influence of ageing

The tendency :

- **Leather #1** is healthy. No evolution of Cr (VI) whatever the ageing conditions
- The unsaturated oils in the **leather #2** appear to respond to temperature and UV factors.
- For **leather #3**, the Cr(VI) develops only in presence of light. The Cr(VI) content is accelerated at high temperature (80°C) and at low humidity (20%).
- The add of vegetable tannin don't stop the chromium (VI)'s generation in presence of light (**leather #4**)
- Increase of humidity can decrease the Cr VI amount

For ageing, light is the most important parameter





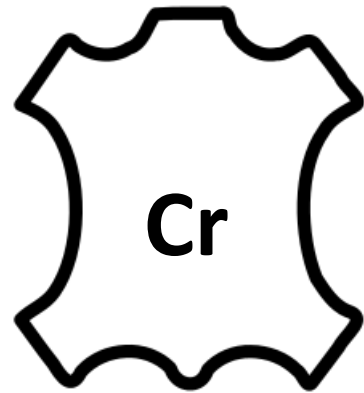
Influence of the tanning process?

Influence of oxygen

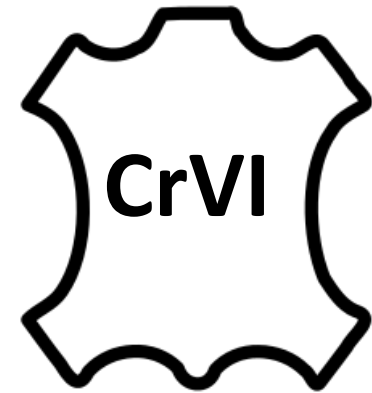
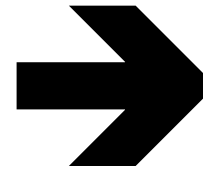


During the ageing tests, some were done under nitrogen atmosphere.

As soon as oxygen is not present no Cr VI appearance is noted.



+ Oxydant Agent?



~~Cr free
Cr Total~~

What nature of Cr is reacting?

Oxygen ↗

Contributing factors :

- Temperature ↗
- Unsaturated fat oil ↗
- UV light ↗
- humidity ↘

Catalytic reaction ?

Double bond + UV + O₂ = oxidation agent

electrochemistry



To Conclude : To avoid Cr VI in leather footwear?

The best solution would be to store the footwear under vacuum, in fridge with ...

Forget it !

... very easy in a Shoe retailer !

More seriously, there is 3 major options :

1. The tanning process shall follow the good practices
2. To understand fully the chemical reaction and to avoid it
3. To work with anti-oxidant chemicals that will stop the action of oxygen

It is be the following steps of our study....

- Thank you for your attention, do not hesitate to contact us

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