Study of the variation of chromium (VI) content inside leather

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Abstract

The objective of this work is to validate the numerous hypotheses offered to date concerning the presence of Cr (VI) in leather, to estimate which major parameters have the strongest contributions, and to develop new practices that will help to limit the appearance and/or development of Cr(VI) in leather. An inter-laboratory test (ILT) was organised between all the European laboratories to avoid certain conclusions being challenged by controversies around EN ISO 17075. CTC, in collaboration with CEN TC 289 and IULTCS, piloted the ILT implementing the two methods for future norms, which are expected to be published early in 2017: pr EN ISO 17075-1 (IUC 18-1): colorimetric detection (old method) and pr EN ISO 17075-2 (IUC 18-2): chromatographic detection (new method).
The tanning influence in Cr(VI) development was studied in two lines of inquiry: leathers that contain unsaturated food oils and leathers that have been retanned with vegetable tannins. On the other hand, accelerated ageing processes in climatic chambers acting temperature and relative humidity have been developed to determine their influence in Cr(VI) formation in the leather. Following this study, the test method pr EN ISO 17075-3 (IUC 18-3): "Leather - Chemical determination of chromium (VI) content in leather - Part 3: Thermal pre-ageing of leather and determination of hexavalent chromium" has been prepared, and will be put to public inquiry in 2017.

Keywords: Cr (VI); leather, unsaturated food oils, vegetable tannins, ageing leather test.

1. Chromium (VI) and leather — the current situation

Currently 85% of the leathers in the world are tanned with chromium. The tanning agent used is a basic sulphate of trivalent chromium (Cr(III)). The Cr(III)found in leather is a chemical form that poses no risk to consumer health. However, under certain conditions, a fraction of this Cr(III) can oxidise to hexavalent chromium (Cr(VI)).

Cr(VI) is an allergen, which can cause skin rashes. For this reason, since 1st May 2015, the European Union has introduced a restriction on the quantity of Cr(VI) permitted in leather coming into contact with the skin. The fixed threshold is 3 mg Cr(VI)/kg leather (without volatiles matters). The Analysis is carried out in accordance with ISO EN 17075. Work on this standard has been extensive since 1993.

1.1 Development of standards related to the determination of Cr(VI)

The first standard describing a method for analysing Cr(VI) content was published by the International Union of Leather Technologists and Chemists Society (IULTCS). IUC 18: 1993 described the preparation of the leather by crushing and extraction with a buffer at pH 8, followed by a colorimetric analysis after a characterisation reaction with diphenylcarbazide. The limit of quantitation (LoQ) was given between 2 and 3 mg Cr(VI) per kilogram of leather (mg/kg).

This standard was adopted by Germany, which published it under the reference DIN 53314, and later at the European level, where it was included in EN 420: 1994 (General requirements for safety gloves). The notified bodies responsible for the certification of protective gloves quickly found that this method was not robust, and did not allow such low concentrations to be determined. A corrigendum was introduced and the LoQ was raised to 10 mg/kg.

IUC 18 was revised in 1996 to define the test with greater precision, and again in 2000 to allow the analysis of strongly coloured leathers. Nonetheless, these improvements proved insufficient, and notified bodies continued to apply the LoQ of 10 ppm. In 2003, European standards published the experimental norm CEN TS 14495, a copy of IUC 18: 2000 This text was reproduced in several key regulations (EN 420: 2003, EN ISO 20344: 2004 for safety footwear, German legislation, etc.). The European Commission nonetheless decided that a reduction in the LoQ was necessary.

After several years of work, ISO and CEN jointly published EN ISO 17075: 2007. The major technical data remained close to the initial method, but a number of improvements were made (dye purification cartridge, colorimetric analysis conditions, etc). The changes finally made the application of a LoQ at 3 mg/kg possible.

The subject is still a topic of discussion today, and research organisations, at the request of public authorities, continue to work on the problem. At the end of 2016, the standard will be revised and split into two parts. Further changes are being made to improve reproducibility between laboratories. For example, the leathers will no longer be crushed, but cut. EN ISO 17075-1 will revert to the old method. The new reference method will be EN ISO 17075-2, in which ionic chromatography is the required analytical technique. This is a major development, which reduces the risk of errors (false positives). Interlaboratory validation trials have confirmed the LoQ at 3 mg/kg for both methods. These complex developments serve as a case study, indeed few subjects have generated as much normative or legislative work.

1.2 Previous studies, "good practice"

Several publications have studied and discussed the best manufacturing conditions for minimising the formation of Cr(VI) in leather:

- avoiding the use of oxidizing agents before and after tanning (bleaching agent);
- finishing the process at a pH between 3.5 and 4;
- maturing after tanning;
- rinsing at the end of tanning, and again at the start of the currying process;
- limit or avoid the use of ammonia for the penetration of dyes;
- use of saturated (non-oxidisable) food oils;
- not using chromate pigments;
- use of vegetable tannins in retanning (1 to 3%).

The addition of antioxidants in the wet phase is a complementary method of ensuring compliance with the threshold of 3 mg/kg Cr(VI) in leathers. Many chemical suppliers have antioxidants for sale to the industry

The objective of this work is to validate the numerous hypotheses offered to date concerning the presence of Cr(VI) in leather, to estimate which major parameters have the strongest contributions, and to develop new practices or new substances that will help to limit the appearance and/or development of hexavalent chromium in leather.

1. Cr(VI) and leather, the CTC study

2.1 Is the EN ISO 17075 test standard reliable?

An inter-laboratory test (ILT) was organised between all the European laboratories, to reassess the relevance of this test method, and to avoid certain conclusions being challenged by controversies around EN ISO 17075.

This standard is currently being revised, in particular with the inclusion of a new Cr(VI) detection technique using ionic chromatography. CTC, in collaboration with CEN TC 289 and IULTCS, piloted the ILT implementing the two methods for future norms, which are expected to be published early in 2017:

- pr EN ISO 17075-1 (IUC 18-1): colorimetric detection (old method)
- pr EN ISO 17075-2 (IUC 18-2): chromatographic detection (new method).

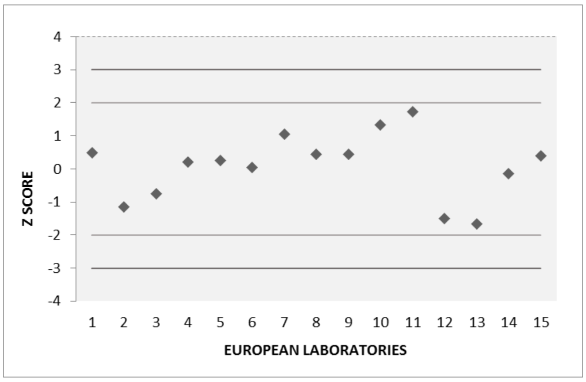


Figure 1: Results of the 2015 inter-laboratory test *(Mean value 3.4 ppm standard deviation of reproducibility 1.1 ppm)*

The results of the ILT (see Figure 1) show that:

- the two methods lead to equivalent results;
- the new method of preparing the leather by cutting improves reproducibility (results between laboratories);
- with a panel of 16 laboratories, the result remains consistent and confirms the previous studies and the applicability of the two methods
- the limit of quantitation remains at 3 ppm with both methods. The homogeneity of the leather, along with its preparation and extraction, remain the critical phases of this method. Although ionic chromatography has many advantages over colorimetry, the ILT revealed no gain in the limit of quantification (recall, the LoQ is the concentration corresponding to a measurement uncertainty of 50%).

Development of Cr(VI) in leather — the influence of tanning

The bibliography raises two interesting lines of inquiry:

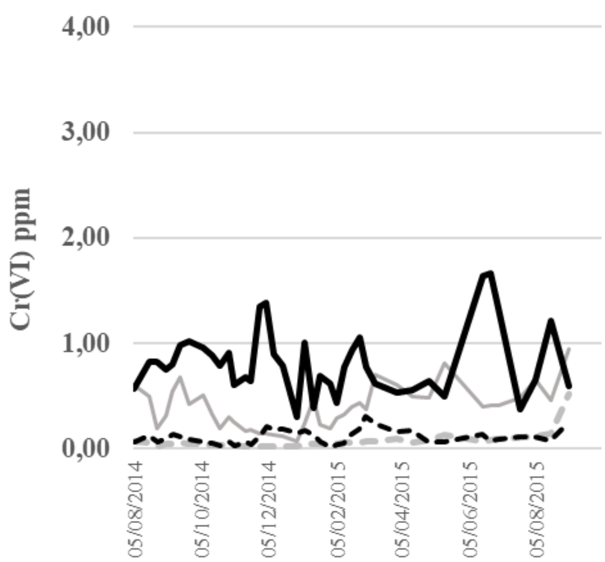
- leathers that contain unsaturated food oils (such as fish oils) appear to be more prone to the development of Cr(VI);
- leathers that have been retanned with vegetable tannins seem less affected by this problem.

It must also be taken into consideration that Cr(VI) levels are not constant over time. All the laboratories found this to be the case, but the parameters allowing the development of Cr(VI) levels with time to be predicted remain to be determined. The Leather Department of CTC has prepared a protocol, starting from a single batch of wet-blue bovine leather:

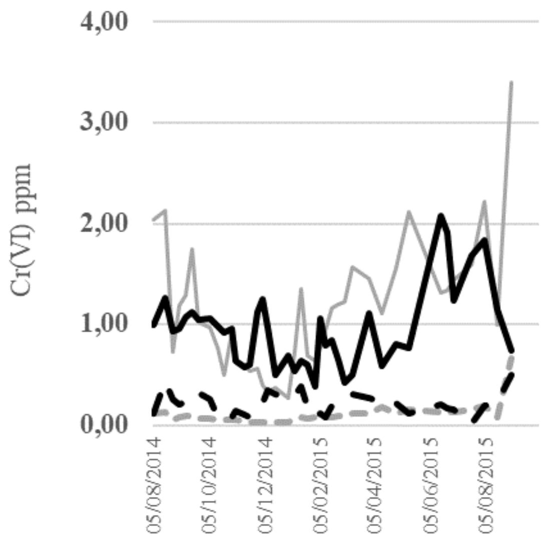
- **leather A**, prepared in accordance with all good tanning practices, with a reducing agent and vegetable retanning. This leather should not therefore develop Cr(VI);
- **leather B**, identical to leather A but using unsaturated food oils (an oxidised and sulphated fish oil);
- **leather C**, prepared in disregard of all good manufacturing practice. This leather should therefore see a development of Cr(VI);
- **leather D**, identical to leather C, but with vegetable retanning.

Each of these leathers was cut in two, longitudinally. One half of the leather was stored in a cold room (protected from light at 4 ±3 °C), the other in the CTC tannery on a frame with no special precautions (exposed to daylight at between 15 and 25 °C, at ambient relative humidity).

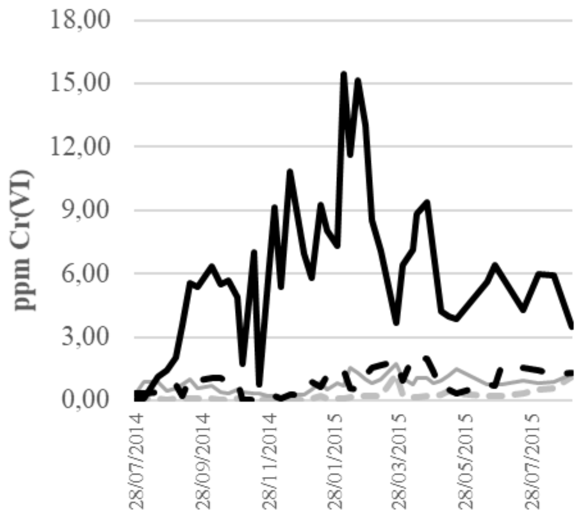
These four leathers were analysed regularly to track the development of Cr(VI) content as a function of time. For each leather, four analyses were made across tannery/cold room leather and crushed/cut leather (see Figure 2).



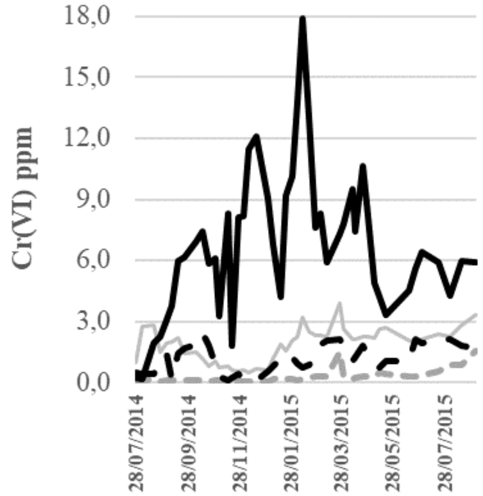
Leather stored in a dark refrigerator at 4 °C then cut



Leather stored in a dark refrigerator at 4 °C then crushed



Leather preserved the tannery in the dark then cut



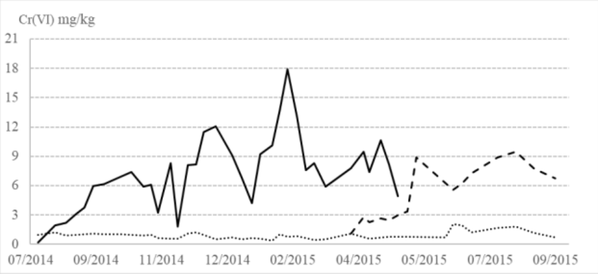
Leather preserved the tannery in the dark then crushed

leather A *leather B* *leather C* *leather D*

Figure 2 *development of Cr(VI) over time in the four leathers*

The first results show that:

- ***leather A**, after more than one year of storage, does not develop, and has never contained, Cr(VI), which confirms the previous studies and confirms the importance of applying good tanning practices (including a reducing agent and vegetable retanning);*
- ***leather B** confirms the potential impact of food oils. Simply using them use (in the absence of reducing agent) leads to the quasi non-compliance of this leather, which oscillates around the 3 ppm mark;*
- ***leather C** developed a significant Cr(VI) content. rinsing during its production was summary and probably yielded a highly heterogeneous leather (hence the fluctuations on the curves as a function of time). This leather, stored in a cold room, developed virtually no Cr(VI). After six months, it was removed from the cold room. A piece of this leather was moved to the CTC tannery platform (ambient temperature, relative humidity and light variations). The Cr(VI) content developed in the same way as the leather at t=0 on the tannery platform (see Figure 3);*
- ***leather D** confirms the beneficial effect of vegetable retanning. Simply using this treatment allows the 3 ppm ceiling to be respected, even thought the rest of the tanning protocol was knowingly defective.*



— In the tannery since 07/2014

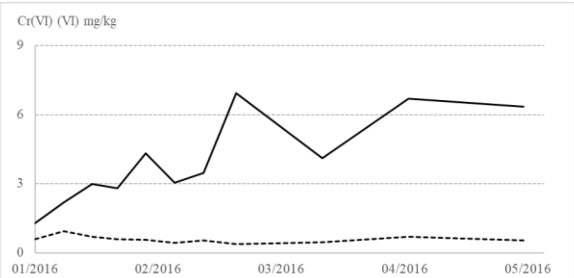
..... In the cold room since 07/2014

-- In the tannery since 03/2015

Figure 3 *Development of Cr(VI) content as a function of storage*

Nevertheless, fluctuations are recorded: vegetable retanning does not solve everything. The results of crushed leathers are almost always superior to those of cut leathers. For the lower Cr(VI) levels (between 0.3 and 4 mg/kg), a difference exists, but remains limited. For samples where the content is more marked, the values determined remain at the same order of magnitude. The study revealed no major effect due to this "sample preparation" parameter.

A similar study was carried out by CTC on reptile leathers (crocodile) the same behaviour was demonstrated (see figure 4)



-- Real time ageing at 4 °C, in the dark

— Real time ageing in the tannery

Figure 4*: the development of the Cr(VI) content depending on storage in a reptile leather*

2.3 Ageing

The Cr(VI) content in a leather is not constant over time, having an upward trend. Manufacturers of leather increasingly wish to be able to predict the development of Cr(VI) levels in their leather products. Such an approach would ensure the compliance of the leather throughout its life cycle. Many European laboratories are working on this problem by simulating an accelerated ageing of the leather over a few hours in climatic chambers, by acting on two factors: temperature and relative humidity. These experiments have shown that a high temperature and a dry atmosphere favour the formation of Cr(VI) in the leather. However, ageing practices are not yet standardised and each laboratory imposes its own particular conditions. Moreover, few currently running studies take into account the influence of exposure to light.

The four bovine leathers (A, B, C, D) were aged under different conditions in a climatic chamber (xenotest), with variations in the following parameters:

- time (24 hours and 48 hours);
- relative humidity (20% and 50% RH)
- temperature (40 °C and 80 °C);
- Light (with and without).

Ageing with the presence of light was performed using an Alpha xenotest.

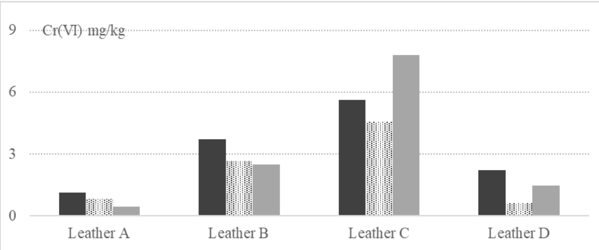
The first results show that:

- **leather A** shows no development and remains below 3 mg/kg whatever the ageing conditions applied. It confirms the importance of respecting good manufacturing practices;
- **leather B** reacts to the high temperature (80 °C) and the dry atmosphere (20% RH) with values greater than 3 mg/kg. The presence of light accentuates the phenomenon and results in the formation of Cr(VI) at a concentration of more than 10 mg/kg.
- **leather C** follows the same trend as leather B, responding to the high temperature (80 °C), the dry atmosphere (20% RH) and the presence of light.
- **leather D** also developed Cr(VI) under the most severe ageing conditions (80 °C, 20% RH, with UV). The addition of a vegetable retanning agent does not seem to completely "neutralise" the formation of Cr(VI).

These tests confirm the influence of the four selected parameters: light, low relative humidity, temperature and time.

On the basis of these accelerated ageing tests, the rest of the study consists of a comparison of these results with 16 months of real-time ageing in the four bovine leathers stored at room temperature at the CTC leather platform.

The objective is to verify that accelerated ageing is indeed representative of the ageing that occurs under "natural" conditions. The comparison of the results is presented in figure 5.



Ageing 40 °C, 20% RH, with UV[redacted]4 h
Ageing 40 °C, 50% RH, with UV[redacted]4 h
Ageing real time, 16 months in th[redacted]annery

Figure 5: *Comparison of accelerated and natural ageing*

A similar trend is observed at 40 °C with the presence of light for 24 hours.
These first results on accelerated ageing demonstrate that light is an important factor, especially on non-finished leather. Tests on other leathers are under way in order to confirm which accelerated leather ageing process is most representative of reality.

2.4 Validation of the new ageing test norm prEN ISO 17075-3

An ILT was organised by CTC in collaboration with CEN TC 289 and IULTCS, with all the laboratories involved in validating the relevance of the test method, and imposing light as an essential parameter.

Conclusions:

- The Interlaboratory trials provided good results, no wrong assessments with 5 leathers 3 preparations and 7 lab (only 2 exclusions for 96 results)
- Thermal effect seems to be slightly more severe but for finished leather the results with Thermal and Light ageing are very close.
- The results for Light Ageing are slightly better than for Thermal Ageing. The dispersion of results for light is smaller.

The method retained provides for leather treatment at 80 °C, with a relative humidity of less than 10% and an ageing time of 24 hours.

Following this study, the test method prEN ISO 17075-3 (IUC 18-3): "Leather - Chemical determination of chromium (VI) content in leather - Part 3: Thermal pre-ageing of leather and determination of hexavalent chromium" has been prepared, and will be put to public inquiry in 2017.

2.5 Leather manufacturing parameters and Cr(VI) content.

Good and bad practices that may have an impact on Cr(VI) content have been published [1]. This study aims to assess the impact of ageing on these practices. Of all the parameters capable of promoting the formation of Cr(VI), not all have an influence. It was essential to evaluate those presenting the maximum risk.

Different practices have been identified and tested:

- ✓ No rinsing after chromium tanning
- ✓ No maturing after chromium tanning
- ✓ No rinsing during wet currying
- ✓ Use of ammonia
- ✓ Use of oxidisable nutrition
- ✓ Finishing the wet process at pH = 5/5.5

and comparisons

- All good practices are respected
- All bad practices are applied

This study was also carried out simultaneously on pickled sheep and cattle skins. Neither production has a dyeing or retanning process.

The results show the skins of sheep and cattle behaving in a similar manner. There is no major difference, it is nevertheless noted that sheep skins tend to develop a little more Cr(VI) under identical conditions in our study. We also tested the influence of ageing at the tannery and accelerated ageing on these leathers (see Figure 6).

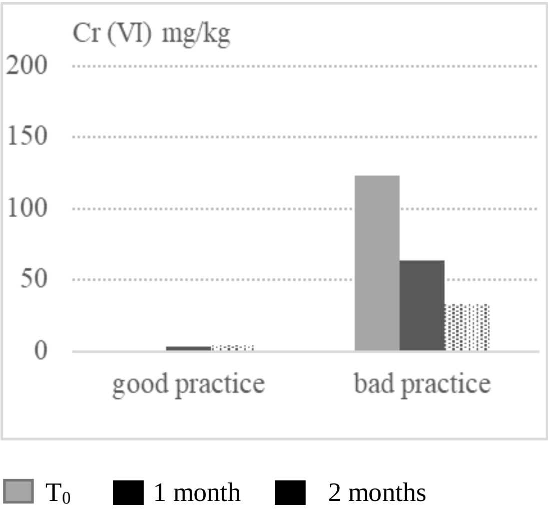
On this "good practice" phase of the study we propose the following remarks:

- At T_0, immediately after manufacture, good practices make it possible to make a leather with no Cr(VI)
- It can be seen that “fat matters parameter: Use of oxidisable oils" is the most important parameter, confirming our starting hypothesis (leathers B and C)

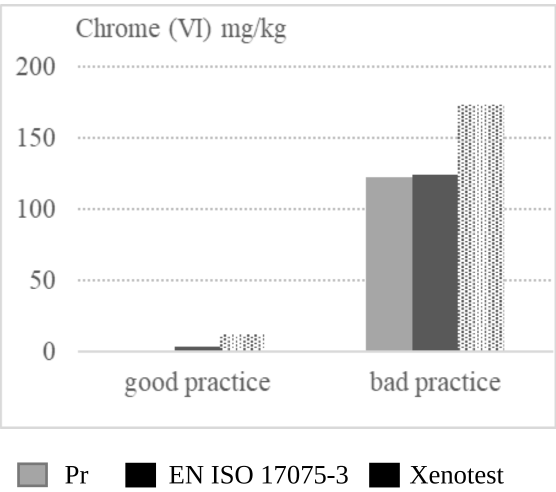
- There is a synergy between the parameters, leather “bad practice” having a higher Cr(VI) content than all the others.
- Light is a critical factor on unfinished leather.
- After ageing (whether accelerated or not), some of leathers produced in this study generate Cr(VI), even with good practice

This last remark is particularly important, it is for this reason that our next investigations will be dedicated for the most part to the study of antioxidants:

- their nature, mineral or organic
- optimal concentrations
- possible combinations



Leather:Sheep Development of Cr(VI) content at tannery

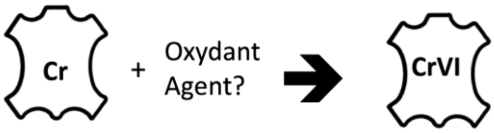


Leather: Sheep Development of Cr(VI) content after accelerated ageing.

Figure 6: *Influence of manufacturing parameters on the appearance of Cr(VI) in the leather*

3. Conclusion

To recapitulate the information obtained during this investigation, we can write a schematic chemical equation:



Our main conclusions:

- Nature of the chromium reaction is currently unknown. In a previous communication[1] we showed that there is no correlation between free chromium or total chromium with the presence of Cr(VI).
- The presence of oxygen is paramount. When carried out under nitrogen, ageing tests revealed no appearance of Cr(VI)
- An increase in temperature favours the appearance of Cr(VI)
- The presence of unsaturated fats appears to be an essential (perhaps even the essential) parameter
- Light also promotes the development of Cr(VI) in unfinished leathers.
- An increase in humidity makes it possible to reduce Cr(VI) levels.[1]

Should a chemical reaction be considered "catalytic" where the unsaturated sites associated with light and oxygen allow the formation of an oxidant capable of reacting with the chromium II in leather?

Upcoming studies on antioxidants should help us to understand these phenomena.

4. References

1. CANNOT JC , BLANC N, FONTAINE M, DEMESMAY D, Study of the variation of chromium VI content inside the leather used in footwear , IUTIC 2016 Chennai