

Prevention of chromium(VI) formation by improving the tannery processes

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Abstract

This work has been funded by the European Commission through the Chrom6less Project (CRAFT -1999-71638).

The objectives of the project were:

- Establishment of the analytical methodology which provided reproducible results that may be free of interferences.
- Identification of the factors that facilitated or impeded the transformation of Cr(III) to Cr(VI).
- Establishment of the best conditions that allowed the production of chromium(VI) free leather, even during the life of the product, in contact with environmental agents such as light or heat.

The following partners participated in the project: Inpelsa, Dercosa, Proquip, Igualada Leather Technology School, CID-CSIC and Miguel Hernandez University, from Spain, Gmelich, Knoll Sitzleder, and Lederinstitut Gerberschule Reutlingen from Germany, and Conceria Il Cigno, Calzaturificio Accademia and Stazione Experimentale from Italy.

Hundreds of samples have been analysed during the project. In order to study the influence of several factors in chromium (VI) formation, a lot of skins/hides have been produced. Several leather articles (hides for clothing, footwear, upholstery, leather goods and furniture upholstery and skins for suede and double face)) have been manufactured free from Cr (VI).

The main results obtained were:

- The new analytical method CEN/TS 14495 has been validated.
- Protective measures for the prevention of chromium (VI) formation have been identified.
- New formulations for several hides/skins have been developed.
- A handbook for the production of chromium (VI)-free leather has been published.

The main conclusions of the project were:

- The Chrom6less Project has shown that most of the skins/leathers did not contain hexavalent chromium.
- It is now possible to confidently determine the Cr(VI) content in all kinds of leather regardless of their colour.
- The application of protective measures developed in the Project allows leather to resist the effect of ageing without the formation of Cr(VI).

The CHROM6LESS Project

The CHROM6LESS Project (Prevention of chromium(VI) formation by improving the tannery processes) is a two-year-long research program (2003-2005) that has involved 11 partners from three European countries. The project has been funded by the European Commission in the thematic programme "Competitive and sustainable growth".

The aim of the Project has been to identify the operations of skin/hide transformation into leather that facilitate or hinder the transformation of Cr(III) to Cr(VI), to determine the most suitable protective measures which prevent this oxidation, and to establish the most suitable manufacturing conditions to allow the production of leathers that are free of hexavalent chromium, even during their useful life in contact with environmental agents such as heat and light.

The participants in this Project are convinced that the tanning with trivalent chromium salts, with an appropriate management of the amounts offered as much as the recovery of the residual chromium in the waste baths is the best state-of-the-art tanning procedure. They are interested in demonstrating that by means of a rational and systematic study, the problem of chromium(VI) is not a relevant complication, and its formation at trace levels may be prevented to fulfil the requirements of the European Eco-label and the German Law.

The Project consortium is summarised in the table.

Partner	Business activity
Inpelsa (Spain)	Manufacturer of lamb skins for clothing. Project Coordinator.
Conceria Il Cigno (Italy)	Manufacturer of hides for footwear
Gmelich Tannery (Germany)	Manufacturer of hides for upholstery
Dercosa (Spain)	Manufacturer of splits for leather goods
Proquip (Spain)	Supplier of chemicals
Knoll Sitzleder (Germany)	Manufacturer of furniture upholstery
Calzaturificio Accademia (Italy)	Manufacturer of footwear
EUETII-Escuela de Tenerife (Spain)	Teaching and research
CID-CSIC (Spain)	Leather research
Stazione Experimentale (Italy)	Leather research
Lederinstitut Gerberschule Reutlingen (LGR) (Germany)	Teaching and research
Universidad Miguel Hernández de Elche (Spain)	Coordinator assistant

Partners in the CHROM6LESS Project

The problem of the analytical methodology

Problem
The procedure DIN 53314, like the former version of the method IUC 18, presents significant difficulties in the analysis of dyed skins/leathers. False positives of chromium(VI) have been reported as a result of the interference of some dyes.

The project partners were concerned about inconsistent and incoherent results from several chromium(VI) analysis and about reports in several media about high percentages of leathers containing chromium(VI). Therefore, they have supported from the beginning the goal of establishing an analytical methodology which provides reproducible results that may be free of interferences.

An inter-laboratory study was developed during the Chrom6less Project Exploratory Award. Several coloured leathers were analysed applying the draft of the new analytical procedure proposed by the CEN/TC Committee.

All participants in the study analysed the same leathers, each one with five replications. The study revealed good behaviour and provided reproducible results between laboratories. Also it was observed that leather colour was no longer a problem. Moreover, the participating laboratories showed to be capable of implementing the new analytical procedure^{1,2}.

Precisely the first result of the project, and one of the most relevant, has been the validation of the analytical methodology after hundreds of analysis, without interference problems. Now it has become clear that the determination of chromium(VI) in all kinds of leather can be carried out with great confidence, regardless of their colour.

Nowadays, this methodology has been approved by the EU as an official Technical Specification and has been named CEN/TS 14495. The detection limit of the method is 10 mg/kg, higher than other methods due to the required dilutions. The International Union of Leather Technologists and Chemists Societies has also updated the former IUC 18 Standard, adopting an equivalent procedure³.

Of course, the CEN/TS 14495 has been applied during the project. Results have been expressed on dry weight. The humidity was previously determined in a different piece of sample than the one used for the analysis. All of the measures were at least duplicated.

Good practices and concrete recommendations to avoid chromium(VI) formation

In the tanning process

Recommendation
Ask the chemical suppliers, mainly from outside the European Union, for a certificate guaranteeing the absence of hexavalent chromium in tanning agents.

In the neutralizing process

Recommendation
Finish wet processes at acidic pHs, between 3.5 and 4, by means of formic acid fixation. Carry out a final washing.

In the retanning process

Recommendation
Use between 1 and 3 % of vegetable tannin extract to provide antioxidant protection.

In the dyeing process

Recommendation
Avoid the use of ammonia prior to the dyeing process.

In the fatliquoring process

Recommendation
Assess the influence of fatliquoring agents of natural origin on the formation of Cr(VI) before use. In leather in which it is not possible to apply a vegetable extract due to the colour change, a 1:1 mixture of a phenolic and an amine antioxidant should be applied because of its protective capacity.

In the finishing stage

Recommendation
Avoid the use of yellow and orange inorganic pigments completely

In the analytical laboratories

Recommendation
Require the laboratories to implement the new official method CEN/TS 14495 for the determination of chromium(VI) in your samples of dyed leather.

Conclusions

The first and possibly the main result of the Project has been the verification of the success of the new CEN/TS 14495 method. After hundreds of analyses carried out in the labs of the participating members, no problems or interferences were detected.

Thus, it is now possible to confidently determine the chromium(VI) content in all kinds of leather, regardless of their colour.

The Chrom6less Project has shown that most of the skins/leathers do not contain hexavalent chromium.

In more than 99 % of the skins/leathers produced and analysed in this European Project, not subjected to accelerated ageing treatments, Cr (VI) was not detectable.

In the few remaining cases in which hexavalent chromium was detected, the reasons were identified. Currently, according to the results of this Project, it is easy to avoid these remaining cases in industrial production, by applying the previously explained recommendations.

This means that the estimations and predictions of a high percentage of skins/leathers containing Cr(VI), published a short time ago, were overestimated owing probably to the use of data obtained by a methodology yielding inexact results.

The application of the protective measures developed in the Project allows leather to resist the effect of ageing without the formation of Cr(VI).

It was established that an unsuitable fatliquoring agent can facilitate the formation of hexavalent chromium in skins/leathers subjected to an accelerated ageing. It was also demonstrated that a suitable retanning process can afford lasting antioxidant protection.

One percent of vegetable tanning agent (on wet-blue weight), applied in the retanning process, is sufficient to meet the most demanding specifications. In order to ensure that the leather resists to an accelerated ageing process without forming Cr(VI), the protection conferred by this 1 % will be sufficient for many skins/leathers.

But for other kinds of leather it will be necessary to increase the offer of vegetable extract to 2 – 3 % depending on the fatliquoring agents, the thickness of the skin/hide, the dyeing process and the type of finishing.

The protection obtained by the 1:1 mixture of a phenolic antioxidant and an amine antioxidant is suitable for leather without finishing in which vegetable extract is inapplicable because of the modification of the colour produced.

The use of yellow and orange inorganic pigments must be completely avoided.

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References

1. A.Rius, J.Font, R.Cuadros, S.Cuadros, M.Santiago, E.Verdú, A.Marsal, *Inter-laboratory Study On Hexavalent Chromium Determination In Dyed Skins*. Journal of the American Leather Chemists Assoc., **97(7)**, 261, 2002.
2. J.Font, A.Rius, R.Cuadros, M^aR.Reyes, A.Marsal. *Nuevos avances en los estudios sobre prevención del cromo hexavalente*, Proceedings of the XXVII IULTCS Congress, Cancún (México), 2003.
3. R.Meyndt, C.Hauber, H.-P.Germann: Anmerkungen zur Chrom(VI)-Bestimmung nach IUC 18/CEN/TS 14495. Leder- und Häute Markt 8/9 2004, p. 7-9.