A Simple Test to Determine the Propensity of a Fatliquor to Trigger the Formation of Chromium (VI) in Leather

by

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Abstract

Since the entry into force of the EU Commission Regulation regarding hexavalent chromium in leather articles in 2014, it is of paramount importance to follow good manufacturing practices to ensure the production of leather not only free of Cr(VI) but with no tendency to its formation. The equilibrium between Cr(III) and Cr(VI) in leather can be disturbed under stressful environmental conditions such as light or heat exposure. These factors could trigger the lipid peroxidation of unprotected unsaturated fatliquoring agents, thus leading to the oxidation of Cr(III) to Cr(VI).

Due to the relevance that the oxidation of the fatliquoring agents has in the subsequent Cr(VI) formation, the Propensity Test has been developed and verified as an innovative verifying in-house tool for tanners to verify that each of the fatliquoring agents used in the tannery processes are properly protected against oxidation and thus, that Cr(VI) formation is not triggered.

The method has four simple steps and can be easily carried out in the tanneries' pilot plant. It does not require special equipment or specific apparatus because all the necessary instruments are usually available in any tannery and the skills needed to perform the test are the same that leather technicians use in their day-to-day work, so the implementation cost is practically non-existent.

This work leads to the conclusion that there is a higher possibility of Cr(VI) formation among sheep skins rather than among calf hides. The rechroming process also presents risks regarding Cr(VI) content in leather, however, in this study it has been shown that rechroming does not increase Cr(VI) formation risks when the fatliquoring agents are properly protected against autoxidation. Therefore, using a well-protected fatliquoring agent is mandatory for the purpose of producing Cr(VI)-free leather despite the type of leather.

Introduction

In 2014, the EU Commission Regulation Nº301 regarding the limitation of hexavalent chromium in leather was issued. This has led leather manufacturers to revise and improve the tanning and wet-end processes and it states the relevance of the application of good manufacturing practices in order to prevent hexavalent chromium formation. Since the entry into force of the regulation, contact dermatitis studies carried out in Denmark, which was the country that submitted the hexavalent chromium restriction proposal to the European Union, show that the prevalence of chromium allergy is decreasing. The EU Directive that restricts the presence of hexavalent chromium in leather goods is thought to be playing a central role in this change.[1]

Nevertheless, appropriate prevention measures still need to be carried out by tanneries in order to ensure the production of leather without risk of Cr(VI) formation.

Hexavalent chromium in leather can come from the use of Cr(VI)-containing products, although nowadays this is highly unlikely. Currently, it is much more common for hexavalent chromium to be found in leather due to the oxidation of the non-fixed fraction of Cr(III) used for tanning or retanning.

The reduction-oxidation potential of the Cr(III)/Cr(VI) equilibrium might vary depending on certain conditions. The reaction that oxidizes Cr(III) to Cr(VI) is reversible, and some factors can have an impact in the formation or reduction of the most oxidized state. A relevant parameter is the presence of oxidizing conditions. If pH is too high, the equilibrium reaction is displaced towards Cr(VI) formation, so in certain wet-end processes the pH has to be controlled and adjusted. Free radicals also have potential of oxidizing Cr(III) to Cr(VI). They might come from the lipid peroxidation of unprotected unsaturated fatliquoring agents. In presence of air, a free radical can react with oxygen. Peroxides and peroxide free radicals are then formed, and an oxidation environment is created. The autoxidation of unsaturated lipids is promoted by its exposure to light and high temperatures, specifically under radiation in the UV spectrum.[2, 3]

Some companies have developed fatliquoring formulations that include, among other measures, antioxidant substances in order to help preventing free radical chain reaction. Regarding auxiliary products in a tanning formulation, the use of oxidizing bleaching agents such as hypochlorite or hydrogen peroxide can promote Cr(VI) formation. On the other hand, vegetable extracts, antioxidants and reductive agents can help to maintain chromium in its trivalent state.[4–8]

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Besides light exposure and temperature, another factor that can also catalyze Cr(VI) formation is low relative humidity. A tannery cannot control the environmental conditions the leather will be exposed to once it leaves the factory. However, good manufacturing practices can be implemented to ensure that the produced leather is as well-protected against Cr(VI) formation as possible, regardless of the environmental conditions it might be exposed to in its useful life.[6, 9, 10]

Influence of fatliquoring in Cr(VI) formation

Among all the tanning activities, wet-end processes and specifically the fatliquoring process can have the largest incidence in Cr(VI) formation, especially if the leather has been properly degreased during beamhouse and wet-end processes and its natural fats have been eliminated.[2,11] Historically, iodine index, a marker of the degree of unsaturation of an oil, was proposed as a way to predict propensity to Cr(VI) formation.[6] However, chemical manufacturers have developed fatliquoring agents protected against oxidation, thus the level of unsaturation in a fatliquor is no longer an indicator of the propensity of a leather to form Cr(VI). The degree of unsaturation is only relevant when fatliquors are not protected against oxidation. Furthermore, a validated test method for measuring the iodine index in commercial sulphited or sulphated fatliquors is not available, thus the comparison between such products would not be reliable.[10,12]

A protected fatliquor is created by firstly selecting high-purity, strictly controlled raw materials. The second mainstay is to apply up-to-date processing methods (aeration, sulphation and sulphitation among others) to stabilize the natural oils in order to inactivate the multi-conjugated bonds. The last element is to add synthetic antioxidant mixtures that work as radical scavengers. It is very important that these antioxidants are evenly distributed and properly dispersed along the leather matrix. The antioxidant addition is a process widely used by different commercial companies in order to protect fatliquors from oxidation. Among others, synthetic phenolic lipidic antioxidants (SPAs) are widely used when protecting leather fatliquors, being the antioxidant 1135 (CAS number 125643-61-0) one of the most implemented.[8,13,14]

Testing for Cr(VI)-free raw materials

To produce leather that does not contain hexavalent chromium, ensuring that all raw materials used are free from this restricted substance does not provide enough safety to the tanner. Hexavalent chromium may be formed within the leather by oxidation of free Cr(III) originating from chromium products used for the tanning or retanning [6,11,15–18] once exposed to the environmental conditions mentioned above. Tanners should obtain from their suppliers a declaration stating that the acquired fatliquoring agents are properly formulated and protected against Cr(VI) formation. Be that as it may, it is not always feasible to get this kind of statement, and moreover, a reliable declaration. Taking into account the important role that fatliquors play in the origin of hexavalent chromium in leather, and due to the fact that the classic control methods of such products used in the manufacturing of leather (determination of common parameters like Iodine Index, fatty acid composition, active matter, SO_3) do not provide safety regarding Cr(VI) concern, it is highly advantageous to perform a new test that can be carried out in the same tannery, to check the propensity of fatliquors to trigger Cr(VI) formation.[10]

The Propensity Test is presented as an innovative verifying in-house test for tanners: a test to check that each of the fatliquoring agents that are used in the tanning process are properly protected against oxidation and thus, that Cr(VI) formation is not promoted. This test can be carried out in-house and lasts no more than one workday. The method has four steps. The first one is to select a wet-blue leather from a trusted origin. The second step is to perform a simple wet-end process in a laboratory drum / small scale drum, omitting the retanning and dyeing processes. Only the investigated fatliquor is applied to the wet-blue in the fatliquoring step. Then an ageing test at 80 °C is performed to the crust leather, according to ISO 10195. Finally, the aged leather is analyzed for Cr(VI) by one of the available methods. This test can be useful for the manufacturers of fatliquoring agents and also for tanneries that use chromium as a tanning system.

The final goal of the Propensity Test is to easily detect fatliquors that have a tendency to trigger hexavalent chromium formation in leather, as a quality control tool for selecting appropriated fatliquors among the offers that the tannery receives from its suppliers. It is proposed as a control tool for each lot of fatliquoring agents. This tool could also be used to guarantee Cr(VI)-free leather when a modification of formulation arises, or also for changes in the wet-blue provider.

The risk of any hexavalent chromium detection in the leather production due to the instability of the fatliquors employed, which is related with important economic losses, is avoided.

Experimental

Skins and hides

Five different types of wet-blue skins and hides have been evaluated during the development of the test to ensure that it is applicable to all kinds of leathers. The leathers were selected to cover a wide range of species, and they include two bovine full-grain calf hides with

Catalan origins (references CA and CC), one bovine split (SP) from Germany, one sheep skin (SS) from England and one hair sheep skin from Nigeria (HS). Prior to testing, the leathers were cut in a rectangular shape of 30 cm x 20 cm.

Materials and facilities

The studies presented in this work were carried out in laboratory drums, suitable for small scale trials. Simplex 2 from InoxVic (Spain) were the drums used. The diameter of the drums was 30 cm and the width was 15 cm. The rotation speed was fixed at 38 rpm. The drums are capable of achieving proper temperatures to ensure that the fatliquoring agents are well fixed. Other small appliances are needed to perform the test: a balance with a resolution of 0.01 g, a thermometer able to measure temperature in a range between 10-60° C and a pH-meter to measure the pH of the bath. A portable pH-meter is a very useful tool. Otherwise, pH strips in the required ranges can be used as well. A solution of bromocresol green is required to check uniformity through the cross-section of the leather.

Propensity Test recipe

The procedure for testing a fatliquoring agent can be performed in laboratory drums in one working session.

An initial washing and degreasing step is included for the removal of traces of natural fat that might be present in the leather. As a general precaution for lipid peroxidation and hexavalent chromium prevention, it is advisable to always degrease the leather at the beginning of the test. However, in case a tannery worked with wet-blue leather with less than 3.0% of soluble matter in dichloromethane (according to ISO 4048), or had a record of several results over time below this value, the degreasing part could be excluded.

After that, there is the rechroming step. This process might be avoided if the tannery will use the tested fatliquor in an article that does not involve a rechroming step.

The neutralization process is a key aspect in the recipe. The pH of the bath after the neutralization and before draining the bath shall be in a range comprised between 5.4 – 5.8 and all the cross-section of the leather has to be visually uniform when a small cut is made and a solution of bromocresol green is applied to the cross-section. If the pH is lower than 5.4, the drum should run for an extra 30 minutes and then the pH should be checked again. If a pH of 5.4 is still not achieved, 0.2% of sodium bicarbonate should be added, then the drum should run again and finally, the pH should be checked again. The amount of sodium bicarbonate needed to reach the desired range of pH depends on the particular characteristics of the wet blue used as raw material. Once adjusted in the first run of the Propensity Test for the specific wet-blue consumed, it would be practically constant for the next applications.

The fatliquoring agent along with the auxiliaries have to be emulsified in order to ensure that the fatliquoring penetrates through the entire cross-section of the leather. Once the fatliquoring has been incorporated, it is necessary to fix it with formic acid. To do so, two additions of formic acid are incorporated in the drum, previously diluted in a 1:5 rate. The final pH shall be between the range of 3.5 - 4.0. If at this point the pH is higher than that, an additional 0.2% of formic acid has to be added, then the drum shall run for 20 min and the pH must be checked again to ensure it falls within the range.

After finishing the recipe, leathers have to be removed from the drums and left overnight covered in a plastic wrap on a smooth surface, in order to maintain humidity and to allow for the fatliquor agents to set and properly bond to the leather fibers. The next day, the plastic wrap is retired and the leathers are left to dry overnight.

Table I includes the detailed description and proportions of the recipe.

A commercial blend of ethoxylated C_9-C_{14} alcohols was used as a degreasing agent. As a wetting and emulsifier agent, a synthetic emulsifier based on alkyl sulphates was selected.

Formic acid, sodium formate and sodium bicarbonate were purchased from conventional chemical product providers, as well as the chromium salt, with 33% basicity and 25% Cr_2O_3.

It is advisable to refer the calculation basis of the recipe to a wet-blue humidity comprised between 45 - 55 %. In case the humidity of the wet-blue skin or hide was out of this range, recalculate its weight referred to a humidity of 50%. This is the wet-blue weight that should be computed in the recipe of Table I.

Testing for hexavalent chromium

Once the leathers are dry, the amount of Cr(VI) has to be analyzed in an external laboratory according to official standards such as ISO 17075-1:2017 or ISO 17075-2:2017. Both methods have a Quantification Limit of 3 mg/kg of Cr(VI). To check for the propensity of the fatliquoring to Cr(VI) formation, the leathers shall be exposed to specific ageing conditions such as thermal heating for 24 hours at 80°C, as it is described in the ISO 10195:2018. The stress that these conditions involve might trigger Cr(VI) formation if the fatliquoring agent was not adequately protected against the effects of the autoxidation.

Table I

Recipe to test a fatliquoring agent for propensity to the formation of hexavalent chromium

Process	% of wet-blue weight	Products	°C	Time (min)	Remarks
Washing	200	Water	45		
	0.2	Formic Acid 85% (1:6)			
	0.8	Wetting agent			
	0.5	Degreasing agent		40’	Drain float
	200	Water		3’	Drain float
Rechroming	150	Water	35		
	0.2	Formic Acid (1:6)		10’	Control pH 3.3-3.4
	3.0	Chromium salt 33% basicity 25% Cr_2O_3		90’	
	2.0	Sodium formate (solid)		30’	Control pH 3.8-3.9 Drain float
	200	Water		3’	Drain float
Neutralization	120	Water	35		
	1.6	Sodium formate (1:10)		30’	
	1.0	Sodium bicarbonate (1:10) (temperature not higher than 35 °C)		60’	Divide into 3 additions separated by 4 min. pH 5.4-5.8
					Write down pH. Check for uniform cross section. Drain float.
	200	Water		3’	Drain float
Fatliquoring and Fixation	90	Water	50	5’	
	1.0	Emulsifier agent			
	9.0	Fatliquor to be tested (Emulsified 1:5 with water at 50°C)			Emulsify
	20	Water	50	90’	Clean the main container, funnel and pipes of the drum
	0.7	Formic Acid (1:6)		20’	
	0.7	Formic Acid (1:6)		20’	Check pH 3.5-4.0
					If pH= 3.5-4.0, drain float. Write down pH. If not, add 0.2% more formic acid and drum 20’ more until pH=3.5-4.0
Washing	200	Water		3’	Drain float

It is advisable that all the analysis are performed in a laboratory accredited by ISO 17025:2017. For routine testing purposes once the Propensity Test is implemented in a tannery, the analysis could be carried out in its facilities through the application of the LeatherKit_Cr6 testing method.[19] As the recipe for the Propensity Test does not involve a dying step, the colorimetric analysis of the crust leather does not require discoloration of the extract, thus simplifying the LeatherKit_Cr6 test procedure and its costs, as the solid phase extraction cartridges would not be required.

Once the leathers have been processed and tested for Cr(VI), the fatliquoring agent tested passes the Propensity Test and thereby it is accepted for daily use if Cr(VI) is not detected in the sample above 3 mg/kg after an ageing test. Should the value of Cr(VI) detected be superior to 3 mg/kg, the fatliquoring agent would not be suitable for ensuring a Cr(VI)-free leather production and thus it should be considered a failure.

Apparent density of leather

The apparent density of the crust leather was established following the method described in ISO 2420:2017.

Results and Discussion

Performance of the Propensity Test

The usefulness of the Propensity Test as a tool for discerning whether a fatliquor agent could contribute to the Cr(VI) formation was evaluated by testing five types of wet-blue skins and hides. Ten different fatliquoring agents were tested with each type of wet-blue. The method has been further used as a routine control test for other fatliquoring agents, proving its utility as a control tool.

The composition of the tested fatliquors included a wide variety and it is described in Table II.

Fatliquoring agents F1 to F4 are commercial fatliquoring agents produced in a manner that they are protected against lipidic peroxidation, be it due to the origin of the raw material, the good manufacturing practices or the addition of certain amounts of specific and tailored SPAs, or due to a combination of these three factors as it is explained in the introduction section.[8,13] These fatliquors were acquired from international chemical companies and should presumably lead to low Cr(VI) formation, below 3 mg/kg, even after an ageing test was applied to a leather.

On the other hand, three base oils from risky natural unsaturated raw materials that were not ready to be on the market and were not protected against Cr(VI) formation (F5 - F7) would presumably get positive detections in Cr(VI) content.

Confirming these hypotheses would lead to the conclusion that the propensity test is suitable to determine whether a fatliquoring agent can trigger the formation of Cr(VI).

Three more fatliquoring agents (F8 - F10), with unknown degrees of protection, have also been tested, to determine their risk regarding hexavalent chromium formation.

The active matter is the percentage of all components of the fatliquoring agent, water excluded. It serves as a guide for the formulation process.

Validation of the Propensity Test

The main objective of the Propensity Test is to distinguish fatliquoring agents that are protected against Cr(VI) formation from non-protected fatliquoring agents. Table III shows the Cr(VI) present in the 5 types of leathers when treated with the 10 different fatliquoring agents described in Table II.

For fatliquoring agents F1 to F4, no hexavalent chromium was detected in any of the five different wet-blue leathers after an ageing process. They were a "pass" for each type of leather, as expected, leading to the conclusion that the appropriate protection applied to the fatliquoring agents' formulation by the chemical companies is working properly against lipidic peroxidation. For fatliquoring agents F5 to F7, extremely high amounts of Cr(VI) were found. They were "fail" for each kind of leather, as expected according to the characteristics described in Table II. This indicates that the Propensity Test is useful for testing fatliquoring agents as it can accurately distinguish between fatliquoring agents with or without propensity to form hexavalent chromium.

Table II

Fatliquors tested during the development of the Propensity Test.

Code	Percentage of active matter	Features
F1	50	Auxiliary synthetic fatliquor with dispersing properties
F2	60	Fatliquoring agent, "compound" type, natural/synthetic
F3	70	Fatliquoring agent, natural/synthetic, high antioxidant properties
F4	50	Fatliquoring agent, synthetic. Needs a penetration auxiliary
F5	75	Non-protected concentrated sulphated oil base, vegetable origin
F6	90	Non-protected sulphited oil base, vegetable origin.
F7	85	Non-protected concentrated sulphited oil base, fish origin
F8	70	Commercial sulphited fish origin fatliquor. Unknown degree of protection
F9	70	Commercial sulphated triolein intended for vegetable tanned leather. Unknown degree of protection
F10	50	Commercial sulphated triolein. Unknown degree of protection

Table III

Cr(VI) content in mg/kg of the experiments for the developing of the Propensity Test. Results obtained according to ISO 17075-2:2017, after ageing the leather samples according to ISO 10195:2018.

	Cr(VI) content in mg/kg for each type of leather				
Fatliquor	**CA**	**CC**	**SP**	**SS**	**HS**
F1	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
F2	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
F3	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
F4	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
F5	14.4	15.8	22.0	43.3	21.4
F6	20.3	27.2	40.6	75.6	41.5
F7	28.6	25.4	37.2	64.2	29.8
F8	21.8	19.8	20.7	20.3	21.0
F9	< 3.0	< 3.0	3.0	3.5	5.9
F10	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0

Products F8 to F10 were three fatliquoring agents with unknown degree of protection. After applying the Propensity Test, F10 has been verified as a protected fatliquoring agent as the Cr(VI) results obtained in the crusts of all type of leather were below 3.0 mg/kg. Fatliquoring agent F9 is intended for vegetable leather, thus implying that it might contain some degree of protection against auto-oxidation and rancidity, but this protection is not effective enough to prevent Cr(VI) formation in leathers with an innate tendency to form Cr(VI). F8 was discovered to be not viable to use for leather tanned with chromium.

Then, in order to validate the propensity test, repeatability and reproducibility were studied. The influence of the substrate (origin and species) and the influence of the rechroming process were studied as well.

Intra-day repeatability was calculated by applying the Propensity Test in a grain bovine leather (CC) six times in the same day. The fatliquoring agent tested was F5 and the average results were 18.6 mg/kg of hexavalent chromium, with a relative standard deviation (%RSD) of 12%. Taking into account the fact that this is a test to be applied in a pilot plant, the %RSD appears to be suitable for the degree of protection needed.

Reproducibility was also calculated following a similar way as the repeatability. A grain bovine leather was also tested with fatliquoring F5 in three different days by two different test operators. This time, %RSD was 21%. Despite of the fact that it may seem a high %RSD, the results of the test show that the process is accurate and precise enough for the main goal of distinguishing between the pass or fail character of a fatliquoring agent, and that it maintains the same qualitative character along all the performed tests.

The test has been implemented in the laboratory of a chemical company that produces fat-liquors and good feedback has been received from the staff.

Cr(VI) content depending on the type of leather

Based on the results shown in Table III, it can be inferred that the result of the analysis of Cr(VI) for fatliquors F5 to F8 follows a certain tendency according to the type of leather. Both bovine grain leather (CA and CC) were the two types of leather where lower amounts of Cr(VI) were obtained, even though the same amount of fatliquoring had been applied to all of the leathers during the Propensity Test, as the recipe states. Split bovine leather (SP) obtains slightly higher concentrations, similar to the hair sheep skins (HS). Finally, sheep skin (SS) is the leather with the highest values of Cr(VI), reaching amounts above 40 mg/kg for all the non-protected tested fatliquoring agents. These findings go in line with more than 500 routine analyses that have been performed at A3 Leather Innovation Center during the 2016-2021 period, where it was observed that split hides and sheep skins tend to have higher

Table IV

Apparent Density of the fatliquored leathers. Results obtained according to ISO 2420:2017.

Type of leather	Apparent density range
Grain bovine leather (CA and CC)	600-720 kg/m^3
Split bovine leather (SP)	530-590 kg/m^3
Hair sheep skins (HS)	400-480 kg/m^3
Sheep skins (SS)	400-480 kg/m^3

Cr(VI) detections and therefore those are the types of leather with higher Cr(VI) risk.

The results obtained with the F9 fatliquoring agent highlight a relevant fact. A fatliquor with a medium-low degree of protection can be used for bovine leather tanning, but only fatliquors with the highest degree of protection can be used for sheep skins and split leather.

These results imply that skin origin and structure have a relevant effect on the final Cr(VI) content. All the leather samples went through a degreasing step, as the Propensity Test recipe describes in Table I. However, differences in Cr(VI) content are still visible, thereby indicating that when performing a uniform degreasing step, the remaining traces of natural fats along with the different features specific for each skin origin might still have some influence in the final concentration.

The compactness of the fiber structure could also play a role. The ISO Standard 2420:2017 for measuring apparent density in leather was applied to the five different types of leather once the Propensity Test was applied and the results are shown in Table IV.

The parameter of apparent density is used to calculate the theoretical mass that one cubic meter of leather weights. Higher values are related with high compacity leathers such as shoe soles, whereas lower apparent densities are linked to more interfibrillar space. Leather samples with lower apparent densities (HS, SS) allow for more air to circulate inside their section. Air contains oxygen, the precursor of lipid peroxidation. The fact of having more interfibrillar space for the air to circulate enables more contact between the oxidizable components of the fatliquoring agents and the oxygen, thereby promoting trivalent chromium oxidation and leading to an increase of Cr(VI) in these samples.

It is also worth noting that when comparing the same breed of animal leather (CA and CC versus SP) there is also a clear tendency for the split bovine leather to obtain higher Cr(VI) values after thermal ageing. The same hypothesis might be applied to this case, as split leather is the part of the bovine leather with less apparent density. Also, split leathers come from the part of bovine hides where it is more likely to find higher amounts of natural grease.

Influence of the rechroming process

The general recipe described for the propensity test involves a rechroming step, as this is a common process to perform when retanning wet-blue leathers for some articles, for example suede splits. However, the rechroming step might not be necessary for other articles and tanners might skip it, thus its effect has been studied.

Rechroming a leather implies the use of more chromium salt, with the risk of increasing the amount of free trivalent chromium present. When there is more trivalent chromium than the collagen can fix, it remains in the interfibrillar space, entailing extra amount of free Cr(III) that is susceptible to oxidation.

The effect of the rechroming step was investigated by performing the Propensity Test with and without rechroming in three types of studied leathers for three protected (F1 to F3) and three non-protected (F5 to F7) fatliquors. According to the results obtained (Table V), Cr(VI) content increases in all the leathers that have been rechromed. It was concluded that the sensibility to detect not well-protected fatliquors is higher for the processes that involve the rechroming, thus confirming the fact that non-fixed Cr(III) can increase Cr(VI) formation when adverse conditions are given.

The study also demonstrates that rechroming has no effect in Cr(VI) formation when protected fatliquoring agents are used in the leather wet-end processes.

Table V

Comparison of the Cr(VI) content in mg/kg of the rechromed and not-rechromed leathers. Results obtained according to ISO 17075-2:2017, after ageing the leather samples according to ISO 10195:2018.

	Influence of the rechroming process. Cr(VI) content in mg/kg.					
Fatliquor	**CC (Bovine)**		**SP (Split)**		**HS (Hair sheep)**	
	Rechromed	**Not rechromed**	**Rechromed**	**Not rechromed**	**Rechromed**	**Not rechromed**
Not protected						
F5	14.4	11.6	22.0	13.0	21.4	14.1
F6	20.3	14.2	40.6	29.4	41.5	30.7
F7	28.6	23.4	37.2	30.3	29.8	28.2
Protected						
F1	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
F2	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
F3	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0

Conclusions

The Propensity Test can be used for detecting fatliquoring agents that are not sufficiently protected against the autoxidation, and therefore they have the tendency to promote the formation of hexavalent chromium when applied to chromium-tanned leathers. It is a simple, economic test that is easy to perform. Such testing presents one clear advantage: the improvement of product and consumer safety as unstable and insufficiently protected fatliquoring agents' batches can be detected at the earliest stage, before entering in the production facilities. The risk of Cr(VI) issues, which is related to important economic losses, is drastically reduced.

This test is easy to carry out in the tanneries' pilot plant. It does not require special equipment. All the necessary instruments are usually available in any tannery. The skills needed to perform the test are the same that leather technicians use in their routine work.

For developing the test, four commercially available protected fatliquoring agents and three non-protected fatliquoring agents were used. When applying the developed recipe, the Cr(VI) amount in each of the applied leathers was found to be matching the expected results. For protected fatliquoring agents, no Cr(VI) was detected above 3 mg/kg, and for non-protected fatliquoring agents, there was Cr(VI) detection which was, in some cases, more than 30 mg/kg.

The test validation has been carried out by assessing the repeatability and reproducibility, with results of 12 and 21 %RSD, respectively. These values are aligned with the expected results for this type of test method. The process is accurate and precise enough for distinguishing between the pass or fail character of a fatliquoring agent and maintains the same qualitative character for all the performed tests.

The risk of finding hexavalent chromium is higher among sheep skins than among calf hides. This outcome is in agreement with the data obtained after the analysis of more than 500 routine samples performed at A3 Leather Innovation Center, that showed that split hides and sheep skins are the types of leather with higher Cr(VI) risk. One of the reasons could be because these are skins with more space between the fibers for the air to circulate. At the same time, this type of leather has an elevated probability of containing traces of natural fats despite being degreased thoroughly along the leather tanning process.

The rechroming process has shown to be a risky process regarding Cr(VI) content in the leather, however, in this work it has been shown that rechroming does not involve Cr(VI) formation risks hazards when the fatliquoring agent is properly protected against autoxidation.

This work also demonstrates that using a well manufactured and protected fatliquoring agent is mandatory for the purpose of producing Cr(VI)-free leather.

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