Use of Long-Chain Synthetic Phenolic Antioxidants to Produce Chromium-Tanned Leather without Risk of Hexavalent Chromium Formation

by

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Abstract

Chromium tanned leather is the widest form of leather tanning across the world, but it might involve a risk of hexavalent chromium formation, which is restricted in leather products above 3 mg/kg. Among other conditions, certain processes might lead to the oxidation of natural fats or fatliquoring agents with unsaturated carbon-carbon bonds, thus generating free radical molecules that can contribute to the Cr(III) oxidation to Cr(VI). The auto-oxidation of unsaturated lipids is promoted by exposure to high temperatures and light, specifically UV radiation. Among other relevant manufacturing practices, the addition of synthetic phenolic antioxidants (SPAs) during the synthesis of fatliquoring agents or during leather manufacturing can be a relevant tool for preventing lipid auto-oxidation.

The efficiency of the long-chain synthetic antioxidant 1135 (AO1135, CAS RN® 125643-61-0) has been assessed for Cr(VI) prevention. The performance of AO1135 has been tested in two different skin types (sheepskin, woolly sheepskin), with two different fatliquoring agents (unprotected and protected against oxidation). The protected fatliquoring agent was formulated with AO1135. Also, two commercial products that contain the AO1135 in its formulation have been applied to leathers. Upon completion of the post-tanning process, the leathers have undergone two different thermal ageing processes.

AO1135 has been verified an effective SPA for Cr(VI) prevention and its application during the post-tanning process does not alter the visual aspect of the leathers. Otherwise, if the post-tanning recipe does not contain well-sourced raw materials or Cr(VI) prevention tools, unsaturated fatliquoring agents or natural fats present in the skins can be a cause for Cr(VI) formation.

Introduction

Leather goods have been used for centuries by human beings, and nowadays they still constitute a valuable asset, due to their unique physical properties and their longevity. The process of obtaining leather in order to prevent collagen degradation is the tanning of animal hides, a by-product of meat consumption. In modern life, leather is used to manufacture footwear and clothing articles, handbags and other fine leather goods, automobile seats and upholstery.[1]

Different types of leather tanning have been developed and improved over time. Still, chromium tanning is the most widely used method since its adoption around mid-19th century. Nowadays, it represents 85% of genuine leather production, mainly due to the properties that the trivalent chromium confers to the finished leather: durability, hydrothermal resistance, fastness of the dyestuffs, pleasant feel and look, fullness, etc., but also due to the lower environmental impact of its production along its life cycle.[2,3]

The use of chromium salts during the tanning process might involve an indirect risk of hexavalent chromium formation. Hexavalent chromium could lead to contact dermatitis for the final consumer of leather articles, hence the European Commission issued the Regulation No 301 in 2014 that limits the amount of Cr(VI) present in leather to a maximum of 3 mg/kg. After being active for over four years, studies carried out in Denmark show that the cases of contact dermatitis related to hexavalent chromium have substantially decreased.[4] The 3 mg/kg value is the limit of quantification of this analyte when determined in a leather matrix, which typically contains about four thousand times more free trivalent chromium than hexavalent chromium.

Commission Regulation No 301/2014 brought the need for the implementation of a variety of widespread good manufacturing practices in tanneries that use chromium in their tanning or retanning processes, which allow for Cr(VI) amounts to be below the restricted limit.

1.1 Origins of Cr(VI) in leather - hexavalent chromium containing substances

A source for hexavalent chromium in leather could be the use of Cr(VI)-containing products, such as the use of lead chromate pigments. However, nowadays this practice is obsolete due to the clear and direct risk of Cr(VI) detection in leather.

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Cr(VI) can also originate from the oxidation of free, non-bonded, trivalent chromium, most likely after the exposure to peroxides or peroxide radicals.[5] Other practices that might involve a risk for Cr(VI) formation and further detection in leather are the use of harsh whitening oxidant products, such as bleach, hydrogen peroxide, potassium permanganate or sodium hypochlorite. Those products provide an oxidizing environment which might lead the free non-bonded Cr(III) to oxidize into Cr(VI).[6]

Although hexavalent chromium is not purposely used in leather production at present time, the conversion of unbound Cr(III) in chromium-tanned leather could generate traces of Cr(VI). This is a reaction influenced by different factors related to production and even storage conditions of finished articles.[7] Differently from other ageing processes, the amount of Cr(VI) formed under certain conditions can be reversed, and the present Cr(VI) could usually be reduced simply by increasing humidity.

1.2 Influence of the pH value

The pH value of the leather is another relevant parameter that can interfere with the Cr(III)-Cr(VI) redox equilibrium. pH has to be controlled and adjusted in certain tannery processes. Otherwise, if pH values are too high, the risk of Cr(VI) detection increases as the equilibrium might be displaced towards Cr(VI) formation.[6,8,9]

For a finished chromium-tanned leather, the most common pH range is usually within the range 3.5 – 4.5. In the market there are also restrictions regarding to pH value for leather from international organizations such as the AFIRM Group, which stablishes the range between 3.2 – 4.5.[10] The common pH range and the values listed by AFIRM are a compromise between the prevention of Cr(VI) formation and the optimization of dying fastness, which are aligned; and also acidic dermatitis in some customers, which increases as a consequence of lower pH values in leather; hence the need for establishing the lower limit for pH value.[11-13]

The appropriate regulation of pH is not the only tool for a tanner to prevent Cr(VI) formation. Tanners might implement other measures that minimize the risk of Cr(VI) formation.

1.3 Oxidation of fatliquoring agents

The fatliquoring step is crucial in the wet-end process of leather production. It will give the leather the touch and flexibility required for the final article. Fat is, next to the tanning agent, the most important component of a finished leather besides the fiber structure. With the exception of sole leather, any kind of softer leather contains remarkable amounts [5 - 20 %] of fat. Fat prevents the sticking, gluing or adhesion of fibers to themselves, and it is said that this is the basis of the leather flexibility.[14]

A general overview of the fatliquoring process can be summarized as follows: First, during the fatliquoring step, the mixture of fatliquoring agents is emulsified in warm water with the support of emulsifying additives. Then, the mixture is incorporated in the rotating drum containing leather and water, which has been preheated to facilitate the penetration of the fatliquoring into the leather. After the drum has rotated for a sufficient amount of time, the effect of mechanical action, together with the temperature, will have ensured proper fatliquoring penetration. Finally, the emulsion of the mixture of fatliquoring agents is broken by means of small acid additions which, in turn, allow for the fixation of fats and oils into the leather. A homogeneous distribution might be difficult to achieve both among the surface of the leather and through its cross-section, thus, making sure that the fatliquoring mixture penetrates well and is evenly distributed is of paramount importance to ensure the desired flexibility in the final article.

Among the variety of wet-end processes, and as early as 1997 - 2000, different research conducted independently concluded that the fatliquoring process can have the largest incidence in Cr(VI) formation due to the auto-oxidation of unsaturated lipids.[15-18]

Some raw materials used for fatliquoring agents' manufacture, or also unsaturated natural fats remaining in a leather, can undergo the process of lipid auto-oxidation in the presence of free radicals, especially unsaturated fatty acids. The bis-allylic hydrogen between the double bonds is readily abstracted in presence of a radical, resulting in the formation of conjugated alkenes due to the rearrangement of the double bonds. Atmospheric oxygen can rapidly be added to the carbon-centered radical to form a peroxy radical. The peroxy radical will capture a new bis-allylic proton, forming a hydroperoxide and a new carbon-centered radical on another fatty acid. This process continues with exponential formation of hydroperoxides and conjugated dienes.[19]

Lipid auto-oxidation can be a risky chain reaction process as it might lead to the formation of hexavalent chromium due to the fact that it provides hydrogen peroxides, that can oxidize the unbonded trivalent chromium.[20,21]

Given the relationship between the double bonds of an unsaturated fatty acid and auto-oxidation, the iodine value test was used in the past as a quality control tool for the raw and unprocessed oils used to make fatliquors. However, the iodine value varies along the different processing steps in which a raw oil is converted into a commercial fatliquoring agent. Nowadays, the iodine value of a properly formulated commercial fatliquor has limited value in terms of predicting Cr(VI) formation and should not be used to compare fatliquoring agents.[22]

1.4 Natural extracts as a way for reducing formed Cr(VI)

Vegetable tanning uses natural vegetable extracts for tanning or retanning leather, which are conformed by high molecular weight compounds that bond with the collagen fibers, helping in stabilizing them and preventing skin degradation.

The polyphenol molecules that conform the vegetable extracts can also act as a neutralizer of free radicals, and this is the reason why vegetable extracts can be incorporated in some chromium-tanning formulations. Polyphenols can reduce the hydrogen peroxides formed by lipid auto-oxidation (Section 1.3), thus reducing the probabilities of molecules of free Cr(III) being oxidized.

It is worth noting that the use of vegetable extracts entails a certain risk for a change of color, due to the slight browning that this natural material undergoes, especially if it is exposed to light.[12,23,24]

1.5 Synthetic phenolic antioxidants as a tool for preventing lipid auto-oxidation

The auto-oxidation of unsaturated lipids is promoted by its exposure to high temperatures and light, specifically under UV radiation. The presence of free radicals can eventually oxidize free trivalent chromium to hexavalent chromium, so lipidic auto-oxidation involves a risk of Cr(VI) formation in leather, especially if it is exposed to the aforementioned extreme conditions.[16,19,25]

However, there are ways of protecting a fatliquoring agent during its manufacture in order to prevent its oxidation. First of all, the chemical nature of the fatliquoring agent has an important role on whether it can be easily oxidized. Thus, compounds with double-bonded carbon chains are the ones that entail a higher risk. Some synthetic fatliquoring agents that are based on sulphited or sulphated and partially chlorinated linear carbon chains might involve a lesser risk of oxidation. Also, carefully selecting a quality source of raw materials free from risky impurities and following adequate processing methods of the materials to achieve stabilization can certainly play a role in reducing the probability of oxidation.

In some cases, chemical companies consider the addition of synthetic phenolic antioxidants (SPAs) during the synthesis of fatliquoring agents, besides other practices like the aforementioned careful selection of raw materials and implementing certain stabilization processes. Another approach is to add a commercial product that contains SPAs in its formulation directly in the leather fatliquoring process. These additions can be beneficial to counterbalance and prevent lipid auto-oxidation.

SPAs have been used in several industrial sectors to retard oxidative reactions and lengthen product shelf life. Most of the commercially available SPAs are grouped under the name of primary antioxidants, as they share a main structure conformed by a hindered phenol, which interrupts oxidation by donating the -OH hydrogen. On the other hand, secondary antioxidants usually decompose hydroperoxides into thermally stable compounds. The efficiency of different structures of primary antioxidants has been widely studied in different industries.[25-29]

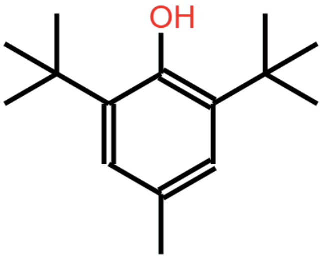

Figure 1. Butylated hydroxytoluene (BHT)

SPAs have been proposed in the past for the leather sector as a mixture of phenolic and amine antioxidants.[12,25] However, it has been found that the shortest synthetic phenolic antioxidant available, the butylated hydroxytoluene (Figure 1, BHT) tends to create a yellowing effect on the substrate it is applied to, due to its conversion to a quinonemethide (CAS RN® 10396-80-2, 2,4-di-tert-butyl-6-ethylidene-2,5-cyclohexadien-1-one) and then to a stilbenequinone (3,3',5,5'-Tetra-tert-butyl-4,4'-stilbenequinone, CAS RN® 809-73-4) [30], [31].

The antioxidant 1135 (AO1135, octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, CAS RN® 125643-61-0) is a synthetic phenolic antioxidant that shows good potential for lipid auto-oxidation prevention in leather and does not have a strong yellowing effect, probably avoided by the longer octadecylpropionate chain attached to the hydroxyphenyl. It has been successfully implemented in different industrial sectors.[26,27,32]

Assessing the ability of SPAs to effectively reduce lipid auto-oxidation rates might be done via several pathways. As mentioned, fatty acid oxidation might involve a light yellowing effect on finished leather, particularly after sunlight exposure. Other sources for detecting oxidized fatty acids could be the rancid smell they release. But the most representative one is Cr(VI) absence or formation due to lipid oxidation in chromium-tanned leathers. This specific indicator can be quantified via Cr(VI) determination in leather, which allows for an accurate conclusion regarding

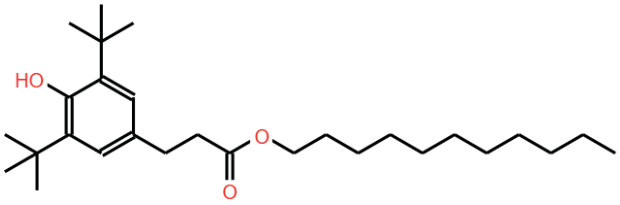

Figure 2. Structure of Antioxidant 1135 (AO1135), octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, CAS RN® 125643-61-0

fatliquoring stability and thus, Cr(VI) protection efficiency, especially if the leather sample has been exposed to some form of ageing prior to the analysis.

Aside from hexavalent chromium determination,[33] there is no other current tool that can indicate whether leather has been treated with SPAs. However, both GC-MS and HPLC-DAD have been used to determine SPAs in different matrixes, such as polyurethane foams, polyamide, wastewater and sludge, among others.[26,34-36]

Finally, the fact that fatliquoring agents, lipidic molecules as they are, need to be properly applied and fixed in order to ensure proper distribution, leads to the idea that synthetic phenolic antioxidants may also require adequate distribution and uniformity when used in a formulation.[14]

1.6 Forcing lipid auto-oxidation in leather

Lipid auto-oxidation can be a natural occurring phenomenon. However, some conditions can either trigger or enhance the radical reaction. Sun light, and in particular, its UV wavelengths, has been proven to be a triggering factor for lipid auto-oxidation in leather, along with heat.[37] Leather that was produced with no apparent initial hexavalent chromium could result in Cr(VI) detection when exposed to sun light or heat.

All these different exposure factors lead to a need for a unified treatment of the sample prior to Cr(VI) determination, in order to assess the tendency of a leather to Cr(VI) formation.

The most widespread pre-treatment for leather samples at the moment is to expose them to continuous heat for a specific period of time. In this line, protocols for leather exposure to these type of stress conditions have been developed. The consolidated ISO standard 10195:2018 describes an ageing process consisting of placing leather samples in an oven at 80°C for 24 hours prior to the Cr(VI) analysis. No other standardized tests have been developed at the moment.

Tanned leather can be stored in a variety of conditions along the supply chain, and such conditions might not be optimal for preventing lipid auto-oxidation. In this work, a new ageing pre-treatment was evaluated as a tool to identify leathers with long-term risk of Cr(VI) formation.

1.7 Determining the efficiency of Antioxidant 1135 to prevent Cr(VI) formation

The main aim of this work is to assess the performance of a long chain lipidic SPA, specifically the AO1135, when applied to leather matrixes as an additive to reduce potential lipidic auto-oxidation that could eventually lead to Cr(VI) formation after being exposed to extreme conditions such as the ones described in Section 1.6. To evaluate AO1135 performance, the approach is to assess its ability to prevent Cr(VI) formation in leather after samples are exposed to conditions that might trigger lipid auto-oxidation (Section 1.6)

1.8 Commercial products with synthetic phenolic antioxidant

There are two main groups of commercial products in the market that contain AO1135. The difference lays in the composition. The simplest way of formulating such products is to dissolve the AO1135 in a solvent, relying on the fatliquoring agent's formulation or other auxiliaries as driver agents for its dispersion and penetration. By contrast, some products contain the AO1135 mixed together with dispersants and emulsifiers so that the emulsion with water and the fatliquoring agent is smooth and good penetration and levelling is ensured along the cross-section and the surface of the leather.

Experimental

Design of the experiment

For assessing the performance of AO1135 in different leather matrixes, two different types of skin origins have been studied. Semi-manufactured wet blue leathers were acquired in an already tanned state, so the difference between the samples laid only in the fatliquoring formulation.

Two different types of fatliquoring agents were assessed. One of them was a fatliquoring agent formulated with a base of sulphited fish oil and with the addition of small amounts of SPA, as well as manufactured according to best manufacturing practices described in Section 1.2. A non-protected fatliquoring agent was used on the second set of leathers.

In order to evaluate the efficiency of AO1135, two commercial antioxidant products (named respectively "Product 01" and "Product 02") that contain this compound were applied to the leathers according to the instructions of the manufacturer. A set of leathers, both with unprotected and protected fatliquors, were treated as a process blank, without the addition of extra amounts of AO1135. Product 01 and Product 02 were selected amongst the increasing variety of commercial products that contain SPAs. Product 01 is a blend of AO1135 with emulsifiers and dispersants, which gives it auto-emulsifyable characteristics that allow for good dispersion along the cross-section of the leather and its surface. Product 02 is a blend of AO1135 with a solvent. In that case, proper penetration and dispersion are ensured by means of adding extra compounds to the mixture or by relying on the fatliquoring agent's auxiliaries. Both products are designed to be applied during the fatliquoring process; emulsified together with the main fatliquoring mixture. The amount applied for each commercial product, according to recommendations of its suppliers, was equal to 0.1% of AO1135 in relationship to the shaved weight of the skin.

Table I

Structure of the study

Type of leather	Type of fatliquoring agent used	Type of extra treatment	Reference
SHEEP-SKIN	Non-Protected fatliquoring agent (U)	Without extra AO1135	01-UB
		With extra AO1135 Product 01	02-U1
		With extra AO1135 Product 02	03-U2
	Protected fatliquoring agent (P)	Without extra AO1135	04-PB
		With extra AO1135 Product 01	05-P1
		With extra AO1135 Product 02	06-P2
WOOLLY SHEEP-SKIN	Non-Protected fatliquoring agent (U)	Without extra AO1135	07-UB
		With extra AO1135 Product 01	08-U1
		With extra AO1135 Product 02	09-U2
	Protected fatliquoring agent (P)	Without extra AO1135	10-PB
		With extra AO1135 Product 01	11-P1
		With extra AO1135 Product 02	12-P2

Table I shows a scheme of all the leather outcomes that were studied.

It has been demonstrated that rechroming a leather might lead to higher Cr(VI) formation when risky fatliquors are used.[38] The unbounded Cr(III) offer is increased in the leather, thus leading to higher chances of oxidation. In this work, all the leathers were rechromed.

2.2 Samples

The risk for Cr(VI) formation is increased if a thorough degreasing process has not been carried out in initial stages of the tanning, as natural fat might lead to lipid auto-oxidation. Good manufacturing practices during tanning are advisable, although in many cases, the early stages of tanning processes (the so-called beamhouse) and the wet end processes take place in different locations. In consequence, they cannot be exhaustively controlled by the intermediate buyer. Taking this information into account, for this study, two types of sheep-skin have been selected and studied.

WS stands for Wooly Sheep-Skin, and these skins belong to an African race of goat. SS stands for Sheep-Skin, also a type of sheep, which usually presents natural fat irregularly distributed. Sheep and wooly sheep-skins, commonly used for shoe or leather goods manufacturing, show higher risk of Cr(VI) formation, probably due to high initial fat percentage and more interfibrillar space.

The wet-end process was applied to the samples, following a simple scheme such as the one described herein.[38] The difference between the samples lies in the fatliquoring formulation, as described in Section 2.1. The process did not involve the application of surface finish coating(s).

It has been shown that the sampled zone of the leather might have an impact on Cr(VI) content.[39] As both types of leather might have higher amounts of natural fats, the Cr(VI) determinations in order to assess the efficiency of each treatment was performed in three zones of the leather; the neck, the flank and the butt, for each of the leathers and processes studied in Section 2.1.

2.3 Chemicals and apparatus

All the chemicals used in the analysis of Cr(VI) were of analytical reagent grade.

Fatliquoring and the rest of wet-end processes have been carried out in common stainless steel pilot plant drums (Simplex 2 from InoxVic, Spain).

The thermal ageing was performed in a DigiHeat TFT drying oven, from Selecta.

2.4 Methods

2.4.1 Method of Cr(VI) determination

The amount of Cr(VI) in leather was determined according to the ISO 17075-2:2017, which has a limit of quantification of 3 mg/kg of Cr(VI). In this case, the analyses were performed in a laboratory accredited by ISO 17025:2015.

2.4.2 Thermal methods to expose the leathers to, prior to Cr(VI) testing

The tanned leathers were tested for Cr(VI) content directly after the fabrication and also after being exposed to certain ageing conditions. The stress of said conditions might trigger Cr(VI)

Table II

Conditions of sample exposure prior to Cr(VI) testing

Thermal ageing	24 h at 80 ºC, <10% of relative humidity (ISO 10195:2018)
Lower-temperature / longer-term ageing	40 days at 40 ºC, <10% of relative humidity

formation if the fatliquoring agents were not adequately protected against the effects of the auto-oxidation, or also if the additional SPAs added in the formulation would not work properly. Thus, the amount of Cr(VI) is a good indicator of the performance of both the fatliquoring agent and the SPA added. If the leather has a content of Cr(VI) above 3.0 mg/kg, the performance of the fatliquoring agent or the AO1135 would not be considered suitable, as this amount of Cr(VI) is above the limit specified in EU Regulation No 301/2014.

To date, the process of thermal ageing described in ISO 10195:2018 is the only official method to test for the propensity of a leather to develop Cr(VI). In order to evaluate alternative methods of ageing and obtain a deeper insight about how Cr(VI) content could evolve, a lower-temperature, longer-term thermal ageing was also assessed. It consisted of keeping the leather samples for 40 days at 40ºC, a condition that could occur if finished leathers are stored in warehouses without temperature control, especially in certain latitudes and hot climates.

Table III

Cr(VI) content according to ISO 17075-2:2017 of Sheep-Skins produced.

Reference	Part of the leather	Cr(VI) content in mg/kg after different exposure to external conditions		
		Initial testing without ageing	Thermal ageing ISO 10195	Lower-temperature / longer-term ageing
01-UB	Shoulder	19.8	43.2	29.4
	Flank	18.6	38.1	22.2
	Butt	17.5	30.8	19.2
02-U1	Shoulder	< 3.0	< 3.0	< 3.0
	Flank	< 3.0	< 3.0	< 3.0
	Butt	< 3.0	< 3.0	< 3.0
03-U2	Shoulder	< 3.0	< 3.0	< 3.0
	Flank	< 3.0	< 3.0	< 3.0
	Butt	< 3.0	< 3.0	< 3.0
04-PB	Shoulder	< 3.0	< 3.0	< 3.0
	Flank	< 3.0	< 3.0	< 3.0
	Butt	< 3.0	< 3.0	< 3.0
05-P1	Shoulder	< 3.0	< 3.0	< 3.0
	Flank	< 3.0	< 3.0	< 3.0
	Butt	< 3.0	< 3.0	< 3.0
06-P2	Shoulder	< 3.0	< 3.0	< 3.0
	Flank	< 3.0	< 3.0	< 3.0
	Butt	< 3.0	< 3.0	< 3.0

Table IV

Cr(VI) content according to ISO 17075-2:2017 of Wooly sheep leathers produced.

Reference	**Part of the leather**	**Cr(VI) content in mg/kg after different exposure to external conditions**		
		Initial testing without ageing	**Thermal ageing ISO 10195**	**Lower-temperature / longer-term ageing**
07-UB	Shoulder	20.5	30.8	23.9
	Flank	19.8	30.7	25.1
	Butt	20.7	29.6	22.1
08-U1	Shoulder	< 3.0	< 3.0	< 3.0
	Flank	< 3.0	< 3.0	< 3.0
	Butt	< 3.0	< 3.0	< 3.0
09-U2	Shoulder	< 3.0	< 3.0	< 3.0
	Flank	< 3.0	< 3.0	< 3.0
	Butt	< 3.0	< 3.0	< 3.0
10-PB	Shoulder	< 3.0	< 3.0	< 3.0
	Flank	< 3.0	< 3.0	< 3.0
	Butt	< 3.0	< 3.0	< 3.0
11-P1	Shoulder	< 3.0	< 3.0	< 3.0
	Flank	< 3.0	< 3.0	< 3.0
	Butt	< 3.0	< 3.0	< 3.0
12-P2	Shoulder	< 3.0	< 3.0	< 3.0
	Flank	< 3.0	< 3.0	< 3.0
	Butt	< 3.0	< 3.0	< 3.0

2.4.3 Determination of natural fat content in leather

The initial natural fat content in wet-blue leather was determined in the wet-blue samples according to ISO 4048:2018. It was verified that the fat content was below 3% for both the wooly sheep and the sheep-skins.

Results

3.1 Cr(VI) content in the tanned leathers

Once all the leathers were manufactured, Cr(VI) content was determined without any previous treatment, and then it was also determined after the exposure of samples to the described conditions.

The specific post-tanning recipes for the 12 leathers can be obtained by contacting the author.

3.2 Dispersion of the Cr(VI) content depending on the different parts of the leather

Being a natural material, leather can show some irregularities or dispersion among fiber distribution, for example, the flank part tends to have more interfibrillar space due to the movements the animal performs during its life. If a fatliquoring agent with auto-oxidation tendencies is unevenly distributed, it could lead to an irregular Cr(VI) content across leather surface.

Three zones were tested for Cr(VI) for each type of leather and process. This lead to the possibility of assessing how disperse the Cr(VI) content can be, even within the same leather, in both sheep-skin and wooly sheep-skins.

Most of the leather treatments led to the non-detection of Cr(VI). Results of the Relative Standard Deviation (%RSD) for the leathers

Table V

Average and %RSD of leathers with Cr(VI) detection

Reference		Variation of the Cr(VI) content in the same leather		
		Initial testing without ageing	Thermal ageing	Lower-temperature / longer-term ageing
01-UB	Average (mg/kg)	18.6	37.3	23.6
	%RSD	6.2	17	22
07-UB	Average (mg/kg)	20.3	30.4	23.7
	%RSD	2.3	2.2	6.4

that were treated with non-protected fatliquoring agents are shown in Table 5.

Discussion

Influence of the fatliquoring agent on the Cr(VI) content, for Sheep-Skin and Wooly sheep leathers

Tables III and Table IV show the Cr(VI) results for all the conditions described in Section 2.1. Both Sheep-Skin and Wooly Sheep-Skin obtain similar results regarding Cr(VI) content when an unprotected fatliquoring agent is applied during the fatliquoring process. In these two cases (References 01-UB and 07-UB), values around 20 mg/kg or higher are obtained. It can be seen that all the leathers treated with protected fatliquoring agents or both commercial synthetic phenolic antioxidants show very good performance against any of the prior ageing treatments applied to them. These results highlight the importance of the quality of raw materials used in the production process.

4.2 Use of synthetic phenolic auxiliaries (AO1135) and its consequences on the Cr(VI) content

When the fatliquoring agent used is not protected, the addition of small amounts of AO1135 has demonstrated to be effective for preventing Cr(VI) formation. This conclusion is extracted from the fact that all the produced leathers with non-protected fatliquoring agents that contained extra additions of AO1135 have successfully prevented Cr(VI) formation, even after being exposed to a conventional thermal ageing process or a soft ageing process.

Results below 3.0 mg/kg of Cr(VI) were obtained with leathers treated with Product 01 and Product 02, even if the leathers were treated with unprotected fatliquoring agents and even after being exposed to the conventional thermal ageing (References 02-U1, 03-U2, 08-U1 and 09-U2), therefore concluding that the two ways of formulating the chemical products are effective for Cr(VI) prevention. Both chemical products, the blend of AO1135 with emulsifiers and dispersants and one with higher AO1135 concentration mixed with a solvent have been demonstrated to exhibit good performance related to Cr(VI) prevention.

When using a fatliquoring agent that included extra protection from the beginning, Cr(VI) content was found to be less than 3 mg/kg in each type of leather. This group of leathers (04-PB and 10-PB) has been useful for assessing the effectiveness of using a commercial product that has been formulated in a way that includes protection against lipid auto-oxidation, thus avoiding hexavalent chromium formation.

If the fatliquoring agent was not protected against auto-oxidation, when those leathers were exposed to thermal ageing, high amounts of Cr(VI) in leather were found, thus restating the aforementioned conclusion.

The results indicate that when using a protected fatliquoring agent or an extra addition of a chemical product that contains AO1135, the Cr(VI) content is below the regulated limit of 3 mg/kg.

4.3 Zone of the leather and Cr(VI) distribution

Cr(VI) distribution was only evaluated in the leathers treated with the unprotected fatliquoring agent, without AO1135 additions, as the Cr(VI) was above 3 mg/kg for all the samples and leather zones (01-UB and 07-UB). Cr(VI) formation according to the tested part of the leather shows higher dispersion in general for Sheep-skins, and lower dispersion for Wooly sheep-skins, although results vary between the range of 2.2 to 22% of RSD.

Several factors contribute to the high values of relative standard deviation obtained. On one hand, it can be seen in Table V that disperse results in Cr(VI) content are linked to a difference in the sampling site, indicating that irregular distribution of the fibers across the leather surface can contribute to uneven Cr(VI) content across the surface. As unbonded Cr(III) oxidation does not depend exclusively on the fiber distribution, other factors have to be balanced in this issue. Fat-liquoring agents are known to be distributed in empty spaces between fibers. This might lead to an increase of Cr(VI) formation due to an exposure to free radicals from the lipid auto-oxidation, if no AO1135 or other SPA additives are added, and it is clear that this phenomenon takes place in references 01-UB and 07-UB.

When using a protected fatliquoring agent or an extra addition of a manufactured chemical product with AO1135 in its formulation, the protection against Cr(VI) is effective no matter the leather zone sampled.

4.4 Effect of different ageing treatments in Cr(VI) content

Two ageing treatments were applied to each zone of the 12 references that had been prepared. Cr(VI) formation has increased for all the leathers after the samples were submitted to the treatments.

The thermal ageing according to ISO 10195:2018 was designed to simulate the propensity of a leather to form Cr(VI) and in this work it has been proven to be an effective method, as Cr(VI) content increased drastically after the treatment in leathers that were not treated with any sort of SPA addition. For leathers treated with SPAs (References 02-U1, 03-U2, 04-PB, 05-P1, 06-P2, 08-U1, 09-U2, 10-PB, 11-P1 and 12-P2), the thermal ageing did not generate Cr(VI) above the regulated limit.

The lower-temperature / longer-term ageing conditions were designed as a simulation of a long-term storage of the leathers. Again, hexavalent chromium in leathers 01-UB and 07-UB clearly increased after the treatment. For the rest of the leathers, the results are not quantifiable because they are below 3.0 mg/kg, the quantification limit of the testing method. The response in the chromatogram appeared to be higher for the aged samples in comparison to the non-aged leather samples, however, the assumption that Cr(VI) had increased cannot be scientifically confirmed.

Conclusions

This study has thoroughly assessed the efficiency of three methods that are currently used for preventing fatliquoring auto-oxidation: using a protected fatliquoring agent that contains a long-chain synthetic phenolic antioxidant (SPA) on its formulation, using an auxiliary product with a specific SPA (AO1135) in a solvent (Product 02), or using a commercial product that contains a SPA (AO1135) amongst other additives such as dispersants and emulsifiers (Product 01). All three options have been proven effective for Cr(VI) prevention, even when the two different types of leather (Sheep-Skin and Wooly Sheep-Skin) were exposed to the conventional thermal ageing (in a laboratory oven at 80°C for 24 h, <10% relative humidity).

Besides the conventional thermal ageing (ISO 10195:2018), another ageing treatment was applied to the 12 produced leathers, in order to evaluate the AO1135 efficiency for a simulated long lasting storage condition in hot climate countries. The treatment showed the same tendency as the ISO Standard.

For each one of the 12 tanned leathers and the different tested conditions, three zones were assessed in order to evaluate Cr(VI) distribution in leather. The percent RSD was between 2.2 and 22%, showing a wide dispersion and leading to conclude that Cr(VI) distribution may depend on many factors, one of which being the natural origin of this particular material and another one, the free radicals generated from the auto-oxidation of unsaturated lipid that unbonded Cr(III) to which the leather might be exposed.

The addition of AO1135 to either the fatliquoring formulation or to the recipe has shown to be a very good tool for hexavalent chromium prevention. Cr(VI) below the regulated limit was achieved when AO1135 was included in some way, even if an un-protected fatliquor was used or if thermal ageing was performed to the leathers, restating the relationship between lipid auto-oxidation and Cr(VI) formation.

Cr(VI) below the regulated limit was achieved when AO1135 was included in some way during the wet-end process. Even if an un-protected fatliquoring agent was used or if a thermal ageing was performed to the leathers, the Cr(VI) content was less than 3 mg/kg if the aforementioned SPA was used. This work leads to two main conclusions: AO1135 is an effective SPA for Cr(VI) prevention and unsaturated fatliquoring agents can be a cause for Cr(VI) formation if the recipe does not contain well-sourced raw materials and/or additional Cr(VI) preventing tools.

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