

INDITEX

Protocol of Good Manufacturing
Processes for the Production
of Chromium(VI)-free Leather

Requirements for suppliers
of leather and fur skins for
footwear (upper, lining and
insole) and bags, to avoid the
formation of Chromium(VI)
in their products

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I. Scope and objective

Requirements for suppliers of leather and fur skins for footwear (upper, lining and insole) and bags, to avoid the formation of Chromium(VI) in their products

Scope

Leather for all kind of footwear and for handbags, handles, knapsacks, shoppers, belt bags, crossbody bags, pouch bags, clutch bags, wallets, card holders and other kinds of bags.

Objective

To provide manufacturing practices to be followed for the production of leather free of Chromium(VI), during all its useful life, even if it comes into contact with stressing environmental agents such as heat, light or low relative humidity.

The following requirements and recommendations work by providing long-time protection against the formation of Chromium(VI). Some measures can be implemented during the beamhouse and finishing stages. However, the core of the effective and durable protection is achieved in the wet-end stage.

It is not uncommon that the tanners deal with wet-blue hides and skins of unknown origin. Sometimes, they do not have the information about how the hides or skins were processed during beamhouse, and despite this lack of information and control, the tanners can and will be able to obtain Chromium(VI)-free leather thanks to the good manufacturing practices applied during wet-end processes.

- [Annex I](#) details the control of the risk associated with and originated from natural fat of skins/hides.
- [Annex II](#) presents an example of statement written by the suppliers of the fatliquoring agents establishing that each one of these products are properly protected against auto oxidation issues.
- Annexes [III](#), [VI](#) and [VII](#) include the description of chemical products that can confer protection against the formation of Chromium(VI) in leather.
- [Annex IV](#) explains in detail the requirement for achieving the pH of leather within the range of 3.2-4.0.
- [Annex V](#) presents an example of a recipe that shows how to apply vegetable extracts correctly.
- [Annex VIII](#) presents the 'Propensity Test', which can be used as an in-house trial for ensuring that a fatliquoring agent does not have the capability to instigate the formation of Chromium(VI).

1) Process Stage: Beamhouse (from raw to tanned)

Recommended good practices

- Thorough degreasing processes must be employed to reduce the presence of natural fats that can potentially contribute to Chromium(VI) formation.
- If bleaching is required (under exceptional circumstance to reduce natural skin pigmentation when producing very pale leather), products with oxidative potential may be necessary. If used, the control of the process should incorporate iodine-starch paper for each batch of leather being processed to check oxidative potential and, if necessary, use a reducing agent prior to adding chromium agents in the tanning stage.
- Obtain test reports from the chemical suppliers of chromium tanning agents demonstrating unquantifiable levels of Chromium(VI), according to ISO 19071 or other appropriate test methods.
- The use of chromium tanning agents recycled by the tannery is prohibited unless tested regularly (at least annually) to confirm unquantifiable Chromium(VI) via ISO 19071 or other appropriate test method for Chromium(VI).
- Final wash after tanning must be employed to remove unfixed chrome to the extent feasible.

2) Process Stage: Wet End

Requirements

- Degreasing during the wet-end is mandatory for skins and splits, and recommended for hides. Please see [Annex I](#).
- Do not employ oxidizing bleaching agents. Do not use hydrogen peroxide or any other peroxide, sodium chlorite or hypochlorite, or potassium permanganate as a decoloring agent after tanning.
- Skins or hides must not be discharged and stored out of the drums at a pH higher than 6.0.
- For fatliquoring, use only products from suppliers that guarantee that they have and implement active protocols to ensure that their fatliquoring agents do not have propensity to the formation of Chromium(VI) in fatliquored hides or skins. Please see [Annex II](#).

[Annex VIII](#) presents the 'Propensity Test' as an in-house trial for ensuring that a fatliquoring agent does not trigger the formation of Chromium(VI).

If a documented Guarantee or a successfully passed Propensity Test is not available for each of the fatliquoring agents employed in the recipe, it is mandatory to employ an antioxidant agent in the fatliquoring mixture. Please, see some examples in [Annex III](#).

- Add formic acid at the end of the wet processes. Use an appropriate amount of formic acid to be sure that the leather has a pH in the range of 3.2 to 4.0 once it is dried, when tested according to ISO 4045 method. Sufficient time should be given to ensure complete penetration of the acid and generate a pH below 4.0 through the entire cross-section of the leather. Wash thoroughly the hides before removing them from the drums. Please, see [Annex IV](#).
- Implement one of the following antioxidant treatments:

- Option a)

Employ a vegetable tanning extract like mimosa, tara or quebracho in the retanning recipe. As a general formula, 5% is recommended. For soft leathers, add 4% of mimosa, tara or sumac. For pastel colours, use 4% of tara. Please, see [Annex V](#).

This option is recommended for glossy leather (full grain, corrected grain leather, embossed leather, coated splits, etc.). It is not recommended for white leather and for leathers with napped texture like velvet splits, nubuck, and suede (*ante*), and for fur skins.

- Option b)

Spray a 40% solution of a liquid reductive agent specifically designed for the prevention and elimination of Chromium(VI) on the flesh side of leathers. For suede leather (*ante*), it should be noted that the reductive agent has to be applied on the grain side.

Apply one coat, at 3-5 g/square foot. For leathers with thickness equal to or above 2.0 mm, apply two coats. Please, see [Annex VI](#).

- Option c)

Spray a 40% solution of a liquid reductive agent specifically designed for the prevention and elimination of Chromium(VI) on the flesh side of leathers. For suede leather (*ante*), it should be noted that the reductive agent has to be applied on the grain side.

Apply one coat, at 3-5 g/square foot. For leathers with thickness equal to or above 2.0 mm, apply two coats. Please, see [Annex VI](#).

- Option d)

Apply an auxiliary lipid synthetic antioxidant agent during the fatliquoring process. Employ the amount recommended in the Technical Data Sheet of the antioxidant product to the fatliquoring mixture. Please, see [Annex III](#).

Options (b), (c) and (d) are appropriate for all kind of leather, including pale color leathers, fur skins, and leathers with napped texture like velvet splits, suede leather and nubuck.

These processes may require further verification and modification or adjustments as per specific characteristics of the final leather article and local environmental conditions.

The implementation of the antioxidant treatments detailed in this document offers a margin of safety. However, the use of such products alone gives no absolute security if the other specific requirements have not been appropriately performed.

Differences between reducing agents and antioxidants:

- Reducing agents are able to eliminate the amount of hexavalent chromium that could exist in the leather in the present moment.
- Lipid antioxidants are used as a preventive tool to prevent hexavalent chromium formation in the future.
- Vegetal extracts are also long-term protectors but they need more quantity to be effective than lipid synthetic antioxidants and affects more the physical properties like light fastness and softness, among others.

Recommended good practices

- During the neutralization process it is recommended to use neutralizing agents with high buffering capacity. In processes where the neutralization pH exceeds pH 5.5, for example to obtain very soft leathers, it is required the use of such buffering neutralizing agents (see [Annex VII](#)).
- The use of ammonia is risky, and the use of other alternative products is strongly suggested, such as the use of efficient dispersant agents. If ammonia is considered to be essential in a particular recipe, precautions must be taken at the end of the fixation step regarding the use of enough amount of formic acid and sufficient rotating time, in order to ensure that the final pH is below or equal to 4.0 through the entire cross-section of the leather. Large final washings are also recommended.

3) Process Stage: Finishing

Requirements

- Avoid the use of the following yellow and orange inorganic pigments in the finishing recipe: C.I. 77600 Pigment Yellow 34 and C.I. 77605 Pigment Red 104. Maintain records of TDS and MSDS of all the yellow and orange pigments used in the tannery as evidence, in case such records were requested by an audit.

Recommended Good Practices

- It is recommended to avoid the use of natural waxes like carnauba in the finishing recipe. It is preferred to replace them by synthetic waxes. Obtain a statement from supplier confirming that finishing oils and waxes are suitable for use and do not contribute to Chromium(VI) formation (such as demonstrating compliance with ZDHC MRSLS specifications).

Requirements for leather subjected to high demands

Some articles like bags can be subjected to longer exposure to direct sunlight and low humidity. If they are made with leathers that do not have a protective finish, such as nubucks or velvety splits, these leathers must have been manufactured with the greatest possible protective actions available.

This means strictly complying with all the measures described in this document, in particular the implementation of lipid synthetic antioxidant treatment. Additionally, it is strongly recommended to apply also a reductive agent.

II. Annexes

Requirements for suppliers of leather
and fur skins for footwear (upper, lining
and insole) and bags, to avoid the formation
of Chromium(VI) in their products

Annex I: Control of the risk associated with natural fat of skins/hides

Avoid the formation of Chromium(VI) related to the risk of natural fat by means of carrying out an appropriate degreasing process at the beginning of the wet-end step. The degreasing requirement does not apply for grain bovine hides (splits are excluded) if a low content of natural fats in the wet-blue hides (less than 3.0% on dry weight) can be proved.

For splits, lamb, sheep, goat and all other type of skins, the degreasing in the wet-end is mandatory, regardless of the degreasing actions previously carried out in the beamhouse process. Follow the instructions of the supplier of the degreasing agent in relation to amount of product employed, temperature of the bath, and drumming time.

The test to determine the fat content of the wet-blue hides is the Standard ISO 4048, *Determination of matter soluble in dichloromethane*. For each source of bovine wet-blue hides (splits not included) used as raw material, if there are two different report analysis of fat below 3.0% (on dry weight), it is not mandatory to carry out a degreasing in the wet-end.

It is necessary to implement a schedule to analyze quarterly the fat content of each source of wet-blue bovine hides to check that the natural fat remains below the 3.0%.

If there are different sources of wet-blue bovine hides (different suppliers or different bovine species), the requirement of <3.0% is applicable for each source.

It is recommended to periodically check the efficacy of the degreasing process by determining the fat content according to the method ISO 4048. As stated before, it should be verified that the natural fat content is below 3.0% for bovine hides (both grain and splits) and below 4.0% for degreased ovine and caprine skins (both on dry weight). This requirement applies to each of the parts of the skins and hides (butt, bellies and shoulder).

Keep records of the following documents for 5 years.

- TDSs of the degreasing agents used
- The part of the recipe that performs the degreasing
- Reports of analysis of total fat content of wet-blues, if available.

Annex II: Example of statement setting that fatliquoring agents are well protected against oxidation issues

Many of the TDS and MSDS of the fatliquoring agents do not report about its antioxidant protection. In these cases, the tannery shall ask for a document issued by its chemical supplier(s) certifying that each fatliquor used in the recipe has the required protection. This is a model for this documentary evidence:

"I hereby confirm that,

The fatliquor xxxxx is suitable formulated and appropriately protected with the antioxidant required by its chemical characteristics, reducing ageing issues and helping to prevent the formation of Chromium (VI).

Signature of the technical manager, or other position in the company"

Keep records of all the certificates for 5 years.

Annex III: Characteristics of the antioxidant auxiliary products to be applied in the fatliquoring mixture

These products are synthetic high molecular weight phenolic antioxidants. They are commercialized as a solvent solution or as an emulsion because they are not water-soluble. They are compatible with the fat-liquor emulsions. Because of that, they are called lipid or lipidic antioxidants.

Application should be carried out by blending the antioxidants with fatliquoring agents before emulsifying them together with warm water and prior addition to the drum. They offer the most efficient protection when applied in the main fatliquoring process.

One of the relevant components of these products is the so-called "Antioxidant 1135" (CAS number 125643-61-0).

There are different suppliers of such products; the availability to supply to all the relevant markets of leather production is guaranteed.

In each case, rigorously follow the instructions of the manufacturer of the product. The optimal amount of antioxidant product to be applied should be evaluated for each particular leather article.

Check that the antioxidant products have not expired, to be sure that they remain effective.

Keep records for 5 years of TDSs and MSDSs of the antioxidant products, and records from the percentage of antioxidant auxiliary employed in the recipes.

Annex IV: Add enough formic acid at the end of wet processes

Adjust the total amount of formic acid added in the recipe in such a percentage that the pH of leather, analyzed according to the Standard ISO 4045 is in the range of 3.2 to 4.0. This should be the usual range for the manufactured leathers. The pH of some batches could exceptionally be above 4.0, but never above 4.5.

For most final articles, this percentage will be comprised between 1.5 and 3.5 % of formic acid of 85% w/w purity, although some leathers may need more amount of formic acid.

Please bear in mind that the small amount of formic acid added to fix the dyestuff in those articles dyed with pale colors is not enough to adjust the pH to 3.2 - 4.0. Higher amounts of acid are necessary.

The total amount of acid should be divided into 2 or 3 additions of formic acid. Drum enough time to ensure complete penetration of the acid and produce a pH below 4.0 through the entire cross-section of the leather.

Keep registers of the pH of final bath for at least 10 lots of each leather article produced.

Store test reports of leather pH (ISO 4048) of at least 10 different production lots for each leather article for 5 years.

Annex V: How to apply the vegetable tanning extract

The use of a vegetable extract in the recipe is one of the options for the antioxidant protection against Chromium(VI) formation. Mimosa is the cheapest option in most markets, but it can be replaced by Tara, Quebracho, Chestnut or Sumac. The protective effect of other vegetable extracts has not been tested.

The following recipe is an example that has to be adapted to the specific characteristics of each particular leather article. For instance, the number, nature and percentages of other retanning agents employed will be different for each article.

Apart from the retanning step, some amount of the vegetable extract could be added at the end of the fatliquoring process.

As a general formula, 5% (or more) of mimosa is recommended for protection purposes. For very soft leathers, use 4% of mimosa, tara, or sumac. Tara extract is more appropriate than mimosa for light color leathers, and gives the same degree of protection against the formation of Chromium(VI).

Keep TDS of the vegetable extract(s) applied, and records of the % of vegetable extract employed in the recipes for each leather article for 5 years.

Process	%	Kg	Products	°C	time (min)	pH/remarks
Retanning / Dyeing	80		Water	30		
	x		Retanning agent 1 (optional)		30'	
	y		Retanning agent 2 (optional)		30'	
	1		Dispersant			
	4-5		Mimosa or Tara or Quebracho or Chestnut or Sumac			
	x		Dye		80'	Check penetration

Annex VI: Characteristics of appropriate reductive agents

These products are mixtures or organic acids of reductive properties. Most of them include in their composition ascorbic acid (CAS number 50-81-7) or iso-ascorbic acid (CAS 89-65-6). They are very soluble in water. Some of the products available in the market are designed to be applied at the end of the wet-end process. Some other products are intended to be diluted and applied by spray gun in the finishing process.

There are different suppliers of such products. The availability to supply to all the relevant markets of leather production is guaranteed.

Check that the reductive products have not expired to be sure that they remain effective.

In each case, follow rigorously the instructions of the manufacturer of the product.

Keep TDS of the reducing agent applied, either at the end of the wet-end or by spray gun for 5 years.

Annex VII: Description of the neutralizing agents with high buffering capacity to lower the risk of the neutralization process

The recommended neutralizing agents are mixtures of organic salts.

Their most particular feature is the strong buffering effect that allows them to be used as neutralizing agents to raise the pH evenly, progressively, and moderately in the neutralization step.

There are also synthetic tanning agents with a pH buffer action that can be used to moderate the raise of pH in the neutralization step.

These products can be used alone or in combination with the classical neutralization products like sodium bicarbonate and sodium formate.

There are different suppliers of such products. The availability to supply to all the relevant markets of leather production is guaranteed.

In each case, rigorously follow the instructions of the manufacturer of the product.

Keep TDS of these products in case they are used in the recipe for 5 years.

Annex VIII: 'Propensity test'

Test of the propensity of a fatliquoring agent to the formation of Chromium(VI).

Step 1. Fatliquoring of a leather sample

Proceed to fatliquor a sample of a degreased wet-blue hide or skin (Note 1).

Prepare as many samples as different fatliquoring agents need to be tested.

The next table contains a suggested recipe for fatliquoring [Note 2]:

Process	%	Kg	Products	°C	time (min)	pH/remarks
Wetting and Degreasing	200		Water	45		
	0.2		Formic acid			
	0.8		Wetting agent			
	0.5		Degreasing agent		40'	Drain float
	200		Water		3'	Drain float
Rechroming (Note 3)	150		Water	35		
	0.2		Formic acid		10'	
	3.0		Chromium salt 33% basicity 25% Cr2O3		90'	
	2.0		Sodium Formate (solid)		30'	
	200		Water		3'	Drain float
Neutralization	120		Water	35		
	1.6		Sodium Formate		30'	
	1.0		Sodium Bicarbonate (1:10)		60'	pH 5.5. Check cross section. Drain float
	200		Water		2'	Drain float
Fatliquoring and fixation	100		Water	50	2'	
	1.0		Anionic emulsifier			
	9.0		Fatliquoring agent to be tested (1:5)		90'	
	0.6-0.8		Formic Acid (1:6)		20'	
	0.6-0.8		Formic Acid (1:6)		20'	Check pH 3.5-4.0 Drain float
	200		Water		3'	Drain float

Notes

(1) Please make sure to select a supply of wet-blue hides/skins in which Chromium(VI) has not been detected in previous analyses.

(2) The non-auto-emulsifying fatliquoring agents have to be applied mixed with auto-emulsifying fatliquoring products that have previously passed the test. It is suggested to employ an amount of 5% in the recipe. Apply such a percentage of auto-emulsifying fatliquoring product that ensures that the emulsion has enough stability to let the fatliquoring mixture penetrate into the skin.

(3) Rechroming in the Propensity Test is recommended for all the fatliquors but it is mandatory for the fatliquors used in recipes where rechroming is applied.

Step 2. Drying

Allow the fatliquored skin samples to stand for the night.

Dry as usual.

Step 3. Analysis

Send all the samples of fatliquored skins to an accredited laboratory.

Perform usual Ageing Test for 24 hours at 80 °C and determine Chromium(VI) by ISO 17075-2.

Step 4. Assessment

The fatliquoring agent passes the **Propensity Test** only if the result of the analysis of the sample fatliquored with it is below 2.5 mg/kg of Chromium(VI).

Keep detailed records of the trials carried out as evidences for 5 years.

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