

# Eco-friendly Leather: Chromium Reduction in the Tanning Cycle

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**Abstract:** The leather manufacturing is traditionally responsible for high environmental pollution. Tannery effluent contains, indeed, large amounts of lime sludge, sulfides, acids, toxic metals salts, in particular chromium salts, which are toxic, non-biodegradable and hardly disposable. For this reason, great research efforts are addressed to establish a significantly eco-sustainable and convenient business for companies and to produce high quality leather products. The replacement of current commercial chemical and toxic products with innovative natural/naturalized products and technologies in some crucial phases of the tanning cycle (mainly bating and defatting), can induce an eco-friendly reduction of the needed chromium amount. Leather samples, treated with innovative bating and defatting products and tanned by several different Cr contents, were characterized by SEM-EDS (Scanning Electron Microscopy equipped with Energy Dispersive X-Ray Spectroscopy) and TGA (Thermogravimetric Analysis). SEM-EDS was used to observe the surface and cross-section morphology and to provide a semi-quantitative elemental analysis, while TGA to evaluate the thermal stability and decomposition phases. The compatibility of the innovative products was demonstrated and the environmental impact of the process, performed by the effluents characterization, was effectively improved as a result of a 20% Cr lowering. The use of innovative products and the chromium reduction did not affect the thermal stability, leather morphology and not involve significant differences in the composition.

**Key words:** Leather manufacturing, tanning cycle, Cr reduction, natural/naturalized products.

## 1. Introduction

Leather production via hides and skins processing is a way to enhance recovery of agro-industrial by-products (circular economy). On the other hand, these processes are very demanding on resources and energy (environment). One ton of bovine salted raw hides produce up to 250 kg of finite leather, requiring about 40 m<sup>3</sup> of water and 400-500 kg of reagents, often chemicals [1]. The leather manufacturing provides a negative image of itself mainly because of the environmental impact of tannery wastes [2]. Conventional leather processing methods, indeed, significantly contribute to the pollution. The wastewaters contain non-biodegradable hazardous chemicals (especially chromium), the solid wastes are

hardly disposable and volatile organic compounds are emitted to the atmosphere.

The leather processing involves many phases that modify the physical, chemical and biological properties of the raw skin/hide. The main five phases of the whole tanning cycle are: bating, defatting, tanning, fatliquoring and dyeing. Bating and defatting are part of the preparatory stage that includes all the operations carried out to prepare the hide/skin for tanning. The tanning phase converts them into a stable, dried and flexible material no longer subject to putrefaction; the most common tanning method is based on the use of chromium salts. The post-tanning operations include fatliquoring and dyeing.

The current main environmental, social and economic goals of leather industry are to reduce the environmental impact and/or to develop a chromium-free tanning cycle [3, 4].

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In this work, leather samples processed by bating, defatting and tanning, defined as wet blue, were prepared using different chromium percentages with the purpose to demonstrate that the replacement of the current commercial bating and defatting agents with natural/naturalized products allows a 20% reduction of Cr salts, maintaining the leather high quality standards and workability.

The activities were carried out in the framework of LIFE14 ENV/IT/443 LIFETAN (eco-friendly tanning cycle) project. The overall aim of the project is to substitute some reagents (toxic or from nonrenewable sources) with natural products or from renewable sources. Traditional/standard reagents for bating and degreasing phases were substituted by innovative products:

- bating agent obtained from poultry manure treated according to a European patent [5], and demonstrated in the framework of LIFE10 ENV/IT/365PODEBA (use of poultry dejection for the bating phase in the tanning cycle) project [6-8];
- degreasing agent obtained from lactose via chemical synthesis [9].

## 2. Material and Methods

The commercial and natural/naturalized bating and defatting agents were compared and their influence in the tanning process was examined. Laboratory tests were carried out in rotating stainless steel tanning drums, measuring 300 mm in diameter and 150 mm in width respectively, featuring systems for automation, control and dosage of water and reactants (Fig. 1).

Several tests have been performed with four different chromium salts concentrations: 4%, 5%, 6% and 8% over pelt weight (w/w) with natural/naturalized products. They were compared with standard process (standard bating and degreasing agent and 8% concentration of Cr salts).

In each test with cattle hides, 3 sq. foot pieces of pelt hides with a thickness of 1.8-2.0 mm were processed. These pieces of wet blue cattle hides had



Fig. 1 Laboratory-scale tanning drums.

been prepared for the tanning operation by means of a standard process of soaking, liming and unhairing. After the tanning process, the wet blue leathers were dried and the shrinkage temperature was determined.

Once every stage was completed, a sample of the residual bath and a sample of each one of the obtained wet blue leathers were taken for their characterization. The environmental evaluation was performed by the characterization of the effluents in accordance with international standards. The selected wastewater control parameters and the related standards are: pH (ISO 10523:2008), TKN (Total Kjeldahl Nitrogen), COD (Chemical Oxygen Demand) (ISO 6060:1989), BOD<sub>5</sub> (Biochemical Oxygen Demand after 5 days) (ISO 5815-1:2003) and biodegradability (determined as BOD/COD).

The four wet blue leather samples, tanned with different chromium concentration (4%w, 5%w, 6%w and 8%w), were characterized by SEM-EDS (Scanning Electron Microscopy equipped with Energy Dispersive X-Ray Spectroscopy) and TGA (Thermogravimetric Analysis).

The SEM characterization was used to observe the surface and cross-section morphology of leather samples [3, 10, 11], while the EDS semi-quantitative analysis was performed to provide the leather elemental composition. A LEO 438 VP, equipped with EDS microanalysis Oxford Link ISIS 300 was used. The analysis was performed in variable pressure and back scattered electrons were detected. These conditions allow the samples observation with no need

of pretreatment, avoiding any damages or contaminations. Moreover, the leather samples were enough dry to be directly observed without specific drying treatment. In all samples, the surface and cross-section observation and the semi-quantitative analysis were carried out on different areas to obtain more representative and reliable results.

TGA was performed to evaluate the thermal stability and decomposition phases [10]. A STA 409 simultaneous analyzer (Netzsch, Selb, Germany) equipped with TGA sample carrier supporting an S type thermocouple was used. The samples weight loss was measured (TGA expressed as % weight loss). The first derivative of the TGA (inflection point I.P.) trace represents the weight loss rate DTG (Derivative Thermogravimetric Analysis) (expressed as  $\% \cdot \text{min}^{-1}$ ) and is used for the exact identification of the relative decomposition steps. The analyses were performed on about 150 mg of material, placed in a sample carrier of 3.4 mL in volume, under dynamic inert Ar atmosphere with a flow rate of 100 mL/min and a heating rate of 10 °C/min up to 1,400 °C. The Netzsch TA window software was used for the results data processing.

### 3. Results and Discussion

The environmental evaluation of the process was performed by the characterization of the residual baths both from the bating/defatting stages and the tanning stage, as reported in Table 1.

The residual baths from the innovative bating/defatting stages exhibited a lower conductivity than those from commercial bating/defatting stages. The COD and BOD<sub>5</sub> of effluents from the bating/defatting stage and the tanning stage are higher.

These results can be ascribed to both the chemical composition of the defatting product that is a derivate of lactose, and the improved defatting action of naturalized products. Biodegradability is greatly improved by natural products. TKN is reduced by naturalized products in bating stage, the phases with the higher N load in tanning cycle. Regarding the chromium content of the residual bath, a greater fixation of the chromium to the collagen is observed by using naturalized bating and defatting products, which is observed in the lower chromium content of the residual tanning bath; 620 mg/L versus 740 mg/L, that means a reduction of around 15%. This indication will be the object of future tests at pre-industrial scale. This is an indication of good performance of new products, thus suggesting to investigate the possibility to carry out the tanning processes with lower Cr contents.

Wet blue samples obtained with 4%, 5%, 6% and 8% were characterized. The eco-friendly wet blue leathers showed good physical strength and adequate smoothness, softness, fullness and flexibility.

After drying, the shrinkage temperature was determined in order to verify if the naturalized bating agent can make a better maceration in the cross-section, increasing the diffusion and the transport of the tanning agent within the pelts and, consequently, allow a reduction of chromium concentration maintaining the same leather quality.

The results are reported in Table 2, showing that with the use of the naturalized bating agent, the chromium salts concentration can be effectively reduced in order to achieve a shrinkage temperature of 100 °C, which is considered suitable for the manufacture of footwear and other leather articles.

**Table 1** Characterization of residual baths.

	Bating/defatting agents	pH	COD (mg/L)	BOD <sub>5</sub> (mg/L)	Biodegradability	TKN (mg/L)	Chromium (mg/L)
Effluents from bating/defatting	commercial/commercial	8.64	7,300	1,387	0.19	1,650	---
	naturalized/natural	8.15	14,800	5,290	0.36	880	---
Effluents from 8% Cr tanning	commercial/commercial	5.09	7,700	3,120	0.41	---	740
	naturalized/natural	5.25	11,500	5,260	0.46	---	620

**Table 2 Chromium percentage vs shrinkage temperature of wet blue leather samples.**

Chromium (weight %)	Shrinkage T (°C)
4	93
5	97
6	99
8	103

Regarding to the COD and BOD, these trials show higher values due to the higher defatting effect and the chemical composition of the ecodefating products which is a derivate of lactose, but in this case, the biodegradability of the residual baths is a 70% higher employing the natural innovative defatting agent, as described in LIFE13 ENV/IT/470ECODEFATTING (environmentally friendly natural products instead of chemical products in the degreasing phase of the tanning cycle) project.

About the nitrogen content in the bating/defatting residual baths, the lower values have been got employing the deodorized Laying Hen Manure (PODEBA) and this reduction is higher by using in combination with the ecodefating natural product.

The morphological wet blue leather surface characterization by SEM revealed a homogeneous pores distribution with uniform size (Fig. 2). Some residual salt crystals, mainly in 5% and 4% chromium tanned leather, were observable. These last two leathers showed also deeper pores.

A representative spectrum of the average surface semi-quantitative composition for every sample is provided in Fig. 3. The main result of EDS microanalysis was the reduction of chromium content congruently with the percentage of chromium salts used in the tanning phase.

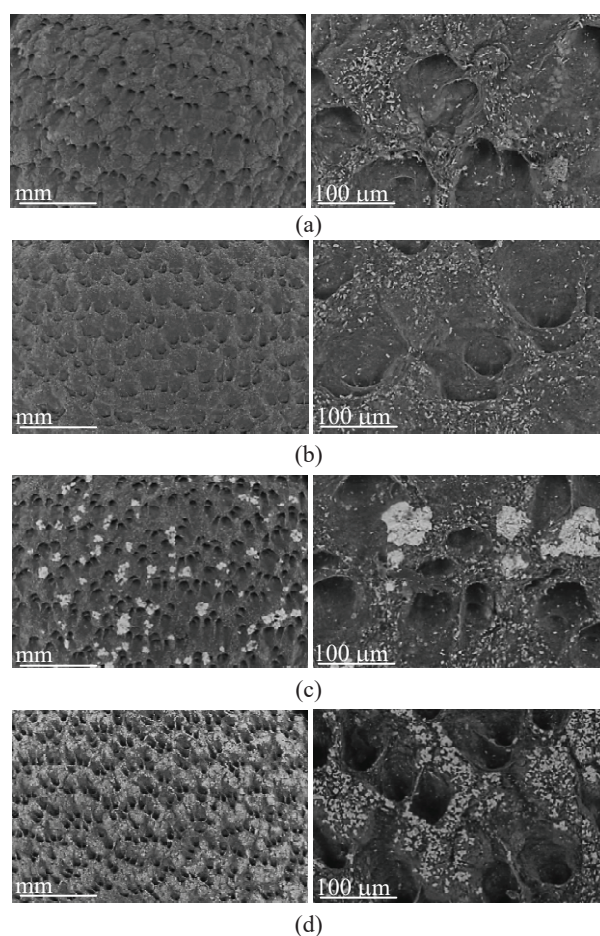
The EDS confirmed the presence of some surface salt crystals, mainly in the case of the 5% chromium tanned leather; the microanalysis restricted to a surface residue highlighted a high content of sodium and chlorine, while the microanalysis restricted to the substrate showed oxygen and carbon as the main elements.

The morphological cross-section characterization highlighted a more compact layer on the sample top

and a more fibrous aspect on the bottom (Fig. 4). The top compact layer was thicker in the 8% and 6% chromium tanned leather than in the 5% and 4% samples; the 4% chromium tanned leathers exhibited a lower thickness. In contrast to the surface, the residues of salt crystals were negligible in the cross-section of all observed wet blue leathers. The cross-section of all observed leathers showed satisfactory opening up extent of fibers, suggesting that post tanning chemicals could easily penetrate into the fibers network.

The EDS microanalysis pointed out, also in the cross-section composition, the reduction of chromium content congruently with the percentage of chromium used in the leather tanning process.

The reduction of Cr content, both in the surface and in the cross-section of Cr-tanned leathers, depending



**Fig. 2** Surface micrographs at different magnifications of 8 (a), 6 (b), 5 (c) and 4 (d) %Cr tanned wet blue leathers.



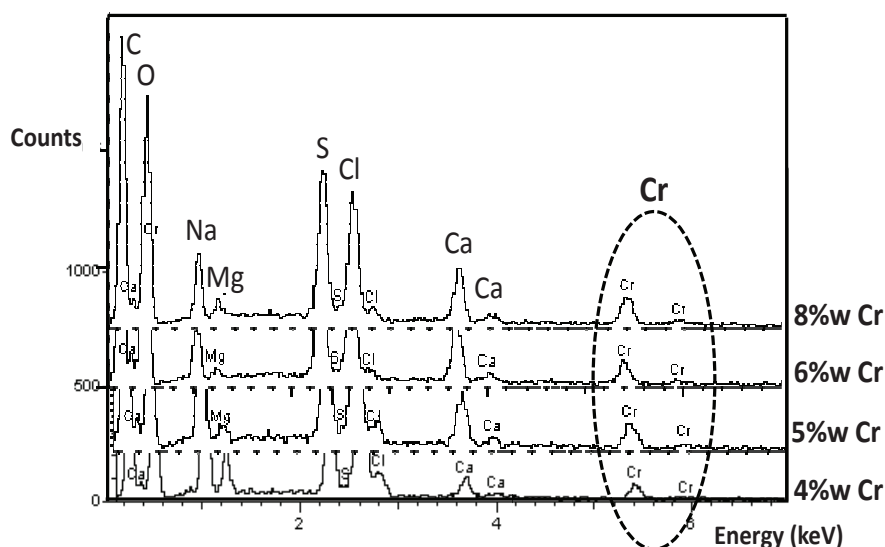


Fig. 3 Typical surface EDS spectrum of wet blue leathers.

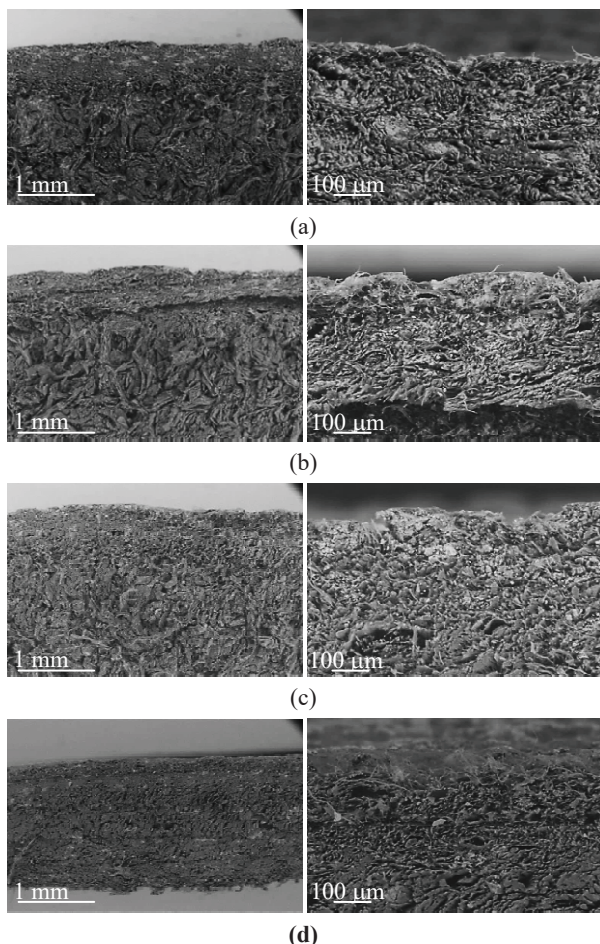


Fig. 4 Cross-section micrographs at different magnifications of 8 (a), 6 (b), 5 (c) and 4 (d) %Cr tanned wet blue leather.

on the amount of Cr used in tanning phase is shown in Fig. 5. A higher Cr content in the leather cross-section than in the surface was revealed in all observed wet-blue samples. The 5% and 6% chromium tanned leathers showed a very similar Cr content, both on the surface and in the cross-section.

The TGA detected similar thermograms for all samples, with four mass loss steps, as confirmed by DTG curve (Fig. 6): 1st step 25-225 °C; 2nd step 225-550 °C; 3rd step 550-850 °C; 4th step 850-1,400 °C.

The first stage of the mass loss is due to the evaporation of the adsorbed or not-structured water which has a maximum degradation rate at around 100 °C; the thermal stability is the same for all samples, except the water percentage. The main step (200-550 °C) corresponds to the decomposition of organic matter and pyrolysis of aliphatic compounds; it was ascribable to the thermal decomposition of collagen. The collagen and elastin constitute the dermis and are the main components of the leather; they are structural proteins made of polypeptide chains whose primary blocks are the amino acids. The collagen structure explains the higher intensity and wider shape of the second DTG peak and the great

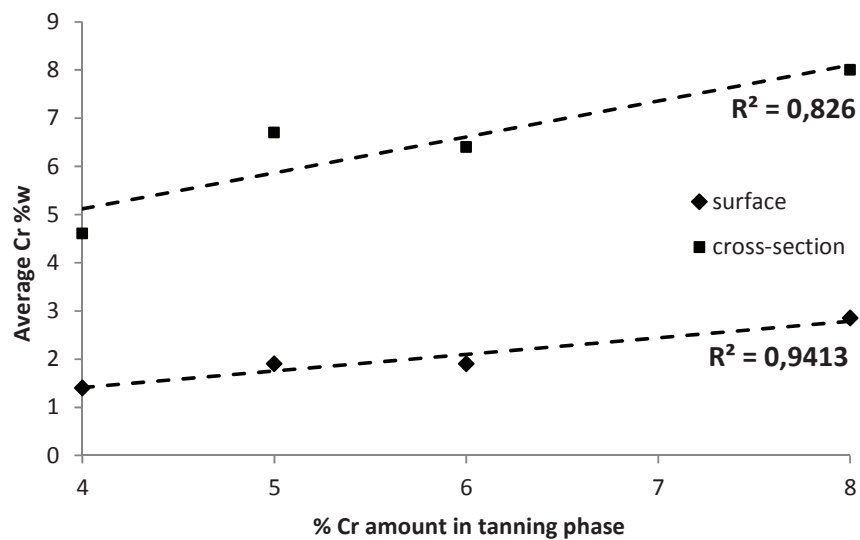


Fig. 5 Comparison between surface and cross-section average Cr content in wet blue leathers.

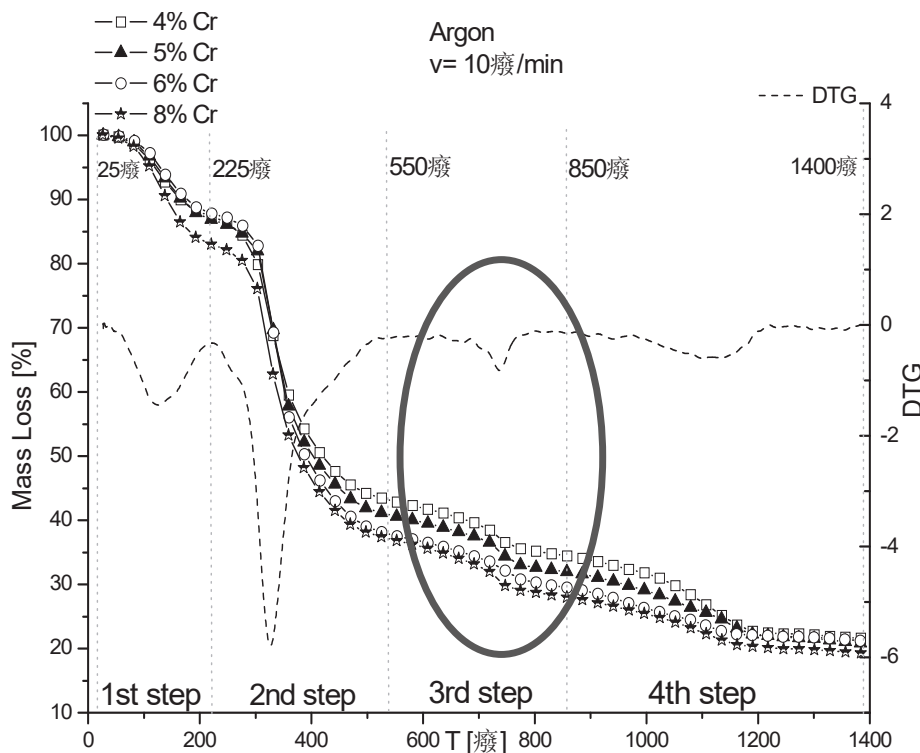


Fig. 6 TGA and typical DTG in argon of Cr tanned wet blue leathers.

mass loss at 200-550 °C. At this evolution temperature range, the decomposition of many products takes place [12]:

- The formation of ammonia from the amino and imino groups of the amino acids of leather occurs at around 300 °C under gradual heating in the thermobalance. The collagen-based materials contain

about 8-13% nitrogen and the formation of significant amount of ammonia, in lines with the expectations;

- At about 300 °C, the scission of the hydroxyl groups (structured water) and the development of CO<sub>2</sub> and SO<sub>2</sub> take place;

- At about 350 °C, it is noticed the presence of molecular ion of acetonitrile and ion of pyrrole. The

main amino acid constituents of collagen are glycine, proline, alanine and hydroxyproline. Pyrrole can be formed from the pyrrolidine rings of proline and hydroxyproline;

- The release of aliphatic alkenyl and alkyl compounds occurs at higher temperatures, in the range 400-550 °C;
- The formation of other molecular compounds occurs: toluene (at about 450 °C), ascribable to the scission of the side groups of phenylalanine, CO<sub>2</sub> and SO<sub>2</sub>, from 300 °C [12].

All these reactions justify the DTG shape between 200 °C and 550 °C, resulting from the overlapping of different decomposition rate peaks. The collagen degradation increases with chromium percentage.

The third mass loss step (550-850 °C) is due to the decomposition of chromium compounds. All analyzed wet blue leathers exhibited a similar mass loss value, thus showing the same thermal stability not affected by the chromium percentage. Therefore, the use of natural/naturalized products in the bating and defatting phases can effectively allow a reduction of chromium amount in the tanning phase.

Moreover, the temperature corresponding to the third DTG peak was about 750 °C and it is also due to the minerals degradation, such as the decomposition of calcium carbonate.

The last step (850-1,400 °C) is attributable to inorganic fraction decomposition; their decomposition occurs around 900-1,000 °C.

During the second mass loss stage, CO<sub>2</sub> is produced and the crosslinked network structure of a macromolecular chain favors the char forming reactions under thermal decomposition in inert atmosphere. Then, the kinetic of the reaction between CO<sub>2</sub> and char was significantly favored at high temperatures, having an exponential dependence on temperature:



It can be assumed that the last peaks of DTG, at about 1,000 °C, were due to this reaction [13].

## 5. Conclusions

A set of wet blue leather samples was analyzed to evaluate the effectiveness of the chromium amount reduction in the tanning phase, even reducing the environmental impact of the process, consequently to the replacement of standard products with innovative natural/naturalized products in the bating and defatting phases. The eco-friendly wet blue leathers showed good physical strength and adequate smoothness, softness, fullness and flexibility.

According to these results, authors can conclude that PODEBA bating agent improves the chrome tanning process and it is possible to use lower concentration of chromium salts (20% less) to obtain the same quality of final leather, measured by means the shrinkage temperature determination.

The most significant considerations to be derived from the SEM-EDS analysis are:

- Both the reduction of chromium content in the tanning phase and the replacement of standard chemical products in the bating and defatting phases, did not significantly affect the leather morphology;
- All the wet-blue leathers showed homogeneous pores surface distribution with uniform size;
- A certain amount of salt crystals residues were clearly visible on the surface of samples;
- The cross-section of all observed leathers showed satisfactory opening up extent of fibres, suggesting that post tanning chemicals could easily penetrate into the fibres network;
- The cross-section was characterized by a two layer structure with a more compact layer on the sample top (thicker in the leathers tanned with higher Chromium amount) and a more fibrous aspect on the bottom;
- The microanalysis pointed out a reduction of chromium content, congruently with the percentage of chromium used in the tanning process, both in the surface and cross-section composition;
- The Cr content was higher in the leather cross-section than in the surface in all observed

samples of the first set (the 5% and 6% Cr tanned leathers showed a very similar Cr content, both on the surface and in the section).

TGA in argon revealed four mass loss steps: evaporation of the adsorbed or not-structured water, decomposition of collagen, chromium compounds and inorganic fraction. All wet blue leather samples exhibited the same thermal stability whatever the chromium percentage is.

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