# Innovative pickle-free chrome tannage: development of the semi-industrial scale process and LCA analysis

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**Abstract:** An alternative pickle-chrome tannage step with a lower inherent potential environmental impact than the traditional one was developed. The innovative process is based on the use of tanning products containing chrome (III) salts with less astringency than the traditional ones. The use of sodium chloride and sulfuric acid is avoided and a significant reduction of chlorides and sulphates dissolved in the exhaust baths is obtained. The technical feasibility of the innovative chrome tannage process was experimentally explored. Several experimental activities have been performed, both on a pilot scale and on an semi-industrial scale, in order to assess the quality of the finished leather obtained by the new pickle-free tanning process. The results have shown that the finished leathers are comparable to the ones obtained by the traditional process in terms of physical-mechanical and technical properties. Besides, a LCA (Life Cycle Assessment) analysis was performed in order to check the actual reduction in environmental burdens due to the process proposed by the authors, in comparison with the traditional pickle-based one.

**Keywords:** chrome tannage; pickle; environmental performance

## 1 Introduction

The tannery wastewaters are characterized by a considerable organic load and high concentrations of inorganic compounds such as chlorides, sulfides and sulphates. The reduction of the effluent production and the decrease of the overall pollutant load are two significant goals to achieve in order to improve the environmental performance of the leather industry.

During the tanning process, sodium chloride and sulfuric acid are required for the pickle step. As a consequence, exhaust baths characterized by high concentrations of chlorides and sulphates are produced and expensive treatments are required in order to remove these pollutants agents.

In the present study, an alternative pickle-chrome tannage step with a lower inherent potential environmental impact than the traditional one was developed. The new process is based on the use of tanning products containing chrome (III) salts with less astringency than the traditional ones. The use of

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sodium chloride and sulfuric acid is avoided and a significant reduction of chlorides and sulphates dissolved in the exhaust baths is obtained, reducing the environmental burdens of the tanning process.

The technical feasibility of the innovative chrome tanning process was experimentally explored. Several experimental activities have been performed, both on a pilot scale and on a semi-industrial scale, in order to assess the quality of the finished leather obtained by the new pickle-free tanning process.

A LCA (Life Cycle Assessment) analysis was also performed in order to check the actual reduction in environmental burdens due to the process proposed by the authors, in comparison with the traditional pickle-based one.

LCA is an internationally standardized method for assessing the environmental burdens associated with a product and/or a process over its entire life from raw material extraction and production, via the use of materials, to waste handling and recycling. For this reason, all the inputs (i.e. energy, material, etc.) and the outputs (i.e. products, waste materials, emissions, etc.) exchanged between a product/process system and the environment must be identified and quantified at each stage of its life cycle. Following the international standard ISO 14040, the LCA analysis consists of four sequential steps: goal and scope definition, inventory analysis, impact assessment and interpretation. In the goal and scope definition are defined the objectives of the study, the functional unit (i.e. the reference unit to which the inputs and outputs are related) and the boundaries of the system (i.e. the extension of the study) in order to construct the product system model. In the Life Cycle Inventory (LCI) the material and energy flows are identified and quantified. In the third step, the Life Cycle Impact Assessment (LCIA), the potential effects caused by the environmental burdens identified in the inventory are assess. The inventory data are assigned to specific, defined impact categories that represent basic environmental issue and their contribution a the category is then evaluated through an equivalence factor that express its effects in relation with a reference parameter. Results are finally normalized to describe their magnitude in relation to background impact that is generally expressed as the average impact per person. The last step mainly consists in the interpretation of the obtained results and in the development of feasible solutions intended to reduce the overall impact.

## 2 Experimental procedures

The pilot-scale runs were conducted on medium calf skins (8-12 kg) in a pilot-scale drum (1 m diameter, 50 cm length). The skins, after soaking, liming, deliming and bating, were divided in two sides: a few sides were chrome tanned traditionally according to the recipe of Table 1, the corresponding sides were submitted to the innovative pickle-free procedure according to the recipe of Table 2. The absolute amount of chrome used in the processes is the same, in order to have the same basis for comparison.

After tanning, the skins followed the traditional re-tanning/dyeing-fatliquoring phases currently used to produce upper leathers.

**Tab. 1 Steps of conventional chrome tanning process (offers: wt.% based on fleshed skin)**

| % | Product | Operations & controls |
|---|---|---|
| 50 | water 20°C | |
| 8 | sodium chloride | |
| 1 | sodium chlorite | Turn 15'/density control 8 Bé |
| 0,6 | formic acid (solution 1:10 w/w) | Turn 40' |
| 1,2 | sulfuric acid (1:20) | Turn 4 h/Drumming overnight |
| | | pH control 2.7-2.8 |
| 4 | basic chrome sulphate | Turn 1 h |
| 0,1 | anti-mould agent | Turn 2 h |
| 4,5 | basic chrome sulphate (26/33) | Turn 5 h |
| 40 | water 40°C | Turn 10' |
| 1 | basifier agent (MgO) | Turn 9 h/Drumming overnight |
| | | pH control 4.1-4.3/Drain |
| 150 | water 20°C | |
| 0,05 | formic acid (solution 1:10 w/w) | Turn 20'/Drain |

**Tab. 2 Steps of pickle-free tanning process (offers: wt.% based on fleshed skin)**

| % | Product | Operations & controls |
|---|---|---|
| 50 | water 20°C | |
| 1 | sodium chlorite | |
| 0.2 | formic acid (solution 1:10 w/w) | Turn 20' |
| 0.2 | formic acid (solution 1:10 w/w) | Turn 20' |
| 0.2 | formic acid (solution 1:10 w/w) | Turn 20'/pH control 5-5.5 |
| 0.5 | chrome alum | Turn 20' |
| 4 | chrome alum | Turn 4 h/Drumming overnight |
| | | pH control 3.8-3.9 |
| 6 | basic chrome sulphate | Turn 3 h |
| 0.1 | anti-mould agent | Turn 5 h |
| 40 | water 40°C | Turn 10' |
| 1 | basifier agent (MgO) | Turn 9 h/Drumming overnight |
| | | pH control 4.1-4.3/Drain |
| 150 | water 20°C | |
| 0,05 | formic acid (solution 1:10 w/w) | Turn 20'/Drain |

The industrial-scale runs were conducted on calf skins (16-20 kg). The skins, after beamhouse phase performed in the tannery, were divided into two sides: a few sides were tanned using innovative pickle-free procedure in pilot-scale drum, the corresponding sides were chrome tanned traditionally in the tannery production line. The pickle-free tanned sides were redelivered to the tannery and reunited to the traditionally ones to follow conventional re-tanning/dyeing-fatliquoring phases.

The final leathers obtained were characterized by their main mechanical and technical properties. Physical testing was conducted according to Italian standards (UNI 10594) for upper leather, while technical properties were assessed by the expertise personnel of PO.TE.CO. The extension and load at tear was determined according to the UNI-ISO 3377-2 method using an electronic dynamometer (Pegasil, Mod. Marte). The data reported are the mean of three determinations. The extension and load at grain crack was determined according to the UNI-ISO 3379 method using a lastometer (Pegasil, Mod. EL-51E). The data reported are the mean of three determinations.

The exhausted floats after tanning were sampled and their sulphates, chlorides and chrome contents were determined.

## 3 Experimental results and discussion

The innovative process is based on the use of chrome alum ($CrK(SO_4)_2{\cdot}12H_2O$). This salt can penetrate into the collagen fibers better than the traditional chrome salts at high value of pH, providing stability to the hide structure. The necessary pH conditions for the traditional chrome tanning agents (basic chrome (III) sulphate) are reached with the acid properties of the innovative chrome salts used. Then, the use of sodium chloride and sulfuric acid is avoided.

The results of the mechanical properties of the crust leathers are reported in Table 3 and 4. The final leather obtained is characterized by physical properties comparable with the conventional crust leather and they comply with the standards required for high quality bovine upper leather.

**Tab. 3 Extension and load at tear of the crust leather obtained on pilot scale**

| Sample | Thickness (mm) | Extension (mm) | Load (N) | Load/thickness (N/mm) |
|---|---|---|---|---|
| Traditional tanning | 1,52 | 35,09 | 115,0 | 75,9 |
| Pickle-free tanning | 1,56 | 40,00 | 118,7 | 76,2 |

**Tab. 4 Extension and load at grain crack of the crust leather obtained on pilot scale**

| Sample | Thickness (mm) | Extension at break (mm) | Load at break (N) | Extension at crack (mm) | Load at crack (N/mm) |
|---|---|---|---|---|---|
| Traditional tanning | 1,55 | 8,05 | 325,64 | 9,94 | 536,81 |

| | | | | | |
|---|---|---|---|---|---|
| Pickle-free tanning | 1,47 | 8,37 | 381,18 | 10,17 | 581,57 |

The results of the assessment of the technical properties of the pickle-free crust leathers, in comparison with the traditional ones, are reported in Table 5. It may be observed that the crust leathers obtained by the pickle-free tanning process and the conventional process show quite similar technical properties. The higher values in opening-up and dyeability performance of the leathers obtained using the innovative procedure could be related with the different degree of masking of chrome salts and to the different reactivity of the obtained wet blues against products used in the following phases.

Table 6 reports the characterization of the exhaust baths of the pickle-free tanning process compared with exhaust bath from traditional process. The evident advantage is a significant reduction of chlorides and sulphates dissolved in the exhaust baths, reducing the environmental burdens of the tanning process. Besides, the content of chromium in pickle-free tanning bath is lower in comparison with the bath from conventional chrome tannage. This result is confirmed by the higher chrome content in skins: 3.2 wt% for skins obtained with traditional process and 4.8 wt% for skins obtained with innovative procedure.

**Tab. 5 Technical properties of the crust leather obtained on pilot scale**

| Technical properties | Traditional tanning | Pickle-free tanning |
|---|---|---|
| Softness | 100 | 100 |
| Fullness | 100 | 100 |
| Opening-up | 100 | 105 |
| Grain blowing | 100 | 100 |
| Dyeability | 100 | 110 |

From the pilot scale run investigations, innovative process without pickle appears a feasible process, either from the environmental or from the technical point of view, to produce high quality bovine upper leather. Following the pilot scale investigation, the feasibility of the process was investigated on industrial scale. The final leather obtained by the innovative process showed good mechanical and technical properties, comparable with those of the traditional tanning, and the leathers were assessed by the expert personnel of the tannery as satisfactory and suitable for their use in the production of high quality upper leathers.

**Tab. 6 Polluting charge of the exhaust bath of the processes**

| Pollutants | Traditional process | Pickle-free tanning process |
|---|---|---|
| Sulphates (mg/l) | 29217 | 9425 |
| Chlorides (mg/l) | 40510 | 838 |
| Total chrome (mg/l) | 5496 | 52 |

## 4 LCA Analysis

### *4.1 Goal and scope definition*

Results have shown that the finished leather obtained by pickle-free tanning process are comparable to that obtained by the conventional chrome tanning in terms of mechanical and technical properties. The LCA methodology was then applied in order to evaluate the actual reduction of the environmental burdens of the innovative process in comparison with the traditional one.

The functional unit was defined as 1 kg of fleshed hides. Considering that the objective of the present study consists in an environmental comparison of two alternative processes, LCA have been accomplished considering only inputs and outputs that change with the alternative. Energy flows, required machineries and ancillary goods remain unchanged and the main differences can be found in the chemicals required at the tannage stage. Figure 1 shows the selected system boundary of the analysis.

### *4.2 Inventory analysis*

Input flows and emission at the tanning phase were collected directly on the field and are summarised in Table 7 (the amount of each chemicals and pollutant is evaluated per kg of fleshed hides). Other data were taken from the Buwal and the Ecoinvent database, both included in the library of the software SimaPro 7.1, which has been used to develop the LCA model.

### *4.3 Impact assessment*

The potential effects caused by the input and output listed in the inventory was assessed with the CML 2 baseline 2000 method. The inventory items are assigned to well defined impact categories, representing specific environmental burdens. The selected method was developed by the Institute of Environmental Sciences of the University of Leiden (The Netherlands) and includes the followings impact categories: Abiotic depletion potential (ADP), Global warming potential (GWP), Ozone layer depletion potential (OLDP), Human toxicity potential (HTP), Fresh water aquatic ecotoxicity potential (FWAEP), Marine aquatic ecotoxicity potential (MAEP), Terrestrial ecotoxicity potential (TEP), Photochemical oxidation potential (POP), Acidification potential (AP), Eutrophication potential (EP).

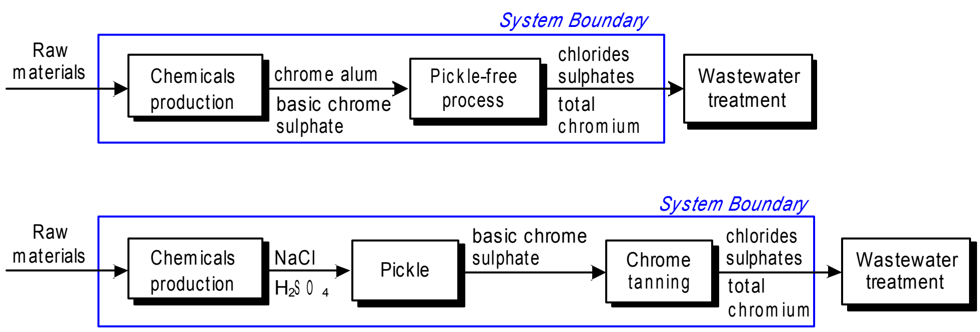


**Fig. 1 Processes flow diagram**

The contribution of each inventory item to the corresponding impact categories is evaluated through a series of equivalence factors, which express effects due to an item in terms of reference parameters. For example, in the "climate change" impact category, $CO_2$ is the reference parameter and the equivalence factor is the Global Warming Potential based on a 100 years lifespan, whose value is 23 for $CH_4$ (i.e. the contribution of 1 kg of $CH_4$ to the global warming is equivalent to the emission of 23 kg of $CO_2$).

The selected method does not take into account chlorides and sulphates as parameters to characterize wastewaters. To fulfill these requirements, a specific equivalence factor was computed in order to express the environmental load of chlorides and sulphates in relation with the limit values of the Italian specifications (D. Lgs. 03/04/2006).

***4.4 LCA results***

Results of the impact assessment step are graphically shown in Figg. 2 and 3. Figure 2 shows, in relative term, which one of the alternative processes has the greatest impact for each impact category. Take for instance the eutrophication category. In this case, the pickle-free process has an impact 0.8 times lower than the traditional one. As can be seen from Figure 2, the innovative process does not presents an environmental impact lower than the traditional one in all impact categories.

As previously noted, for a fair assessment of results, data can be normalized to express their actual magnitude in relation to a known reference value that is the equivalent impact per person (*i.e.* the average annual impact generated by the ordinary activities performed by an individual).

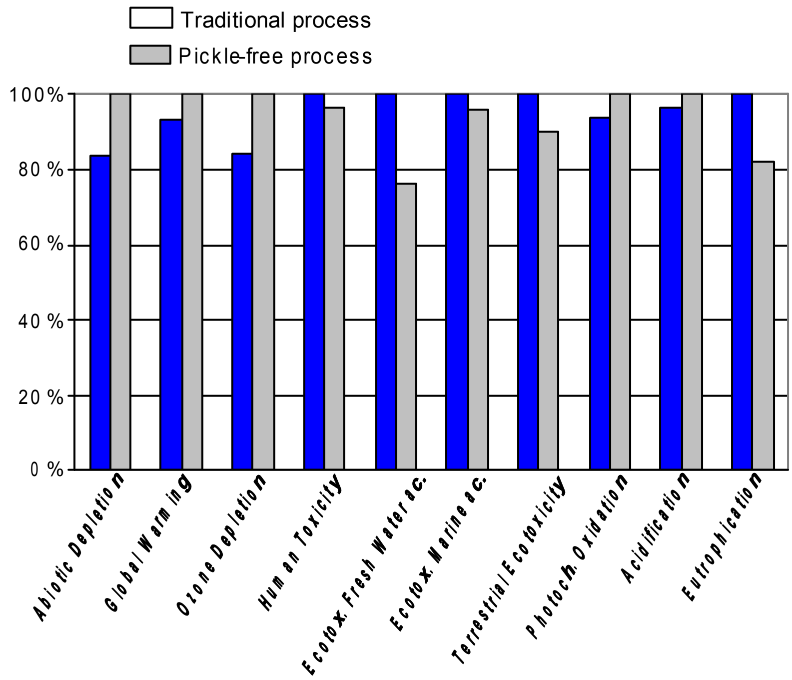


**Fig. 2 Impact assessment results**

**Tab. 7 Input-output of the processes**

| | | Pickle-free process | Traditional chrome tanning |
|---|---|---|---|
| Input | Chrome alum | 0.045 [kg] | 0 [kg] |
| | Basic chrome sulphate | 0.060 [kg] | 0.080 [kg] |
| | NaCl | 0 [kg] | 0.080 [kg] |
| | $H_2SO_4$ | 0 [kg] | 0.012 [kg] |
| Output | Chloride | $8.5 \cdot 10^{-3}$ [kg] | $3.65 \cdot 10^{-2}$ [kg] |
| | Sulphate | $0.75 \cdot 10^{-3}$ [kg] | $2.62 \cdot 10^{-2}$ [kg] |
| | Total chromium | $0.05 \cdot 10^{-3}$ [kg] | $4.95 \cdot 10^{-3}$ [kg] |

As shown in Fig. 3, the impacts categories most significantly affected are "*Fresh water aquatic ecotoxicity*" and "*Marine aquatic ecotoxicity*". It is also evident that the adoption of the pickle-free tanning process makes it possible to reduce environmental burdens in both these impact categories. As far as the other categories are concerned, even if several impacts of the innovative process are greater than the traditional one, their normalized magnitudes may be considered not significant in terms of effects on the ecosystem and on the human health.

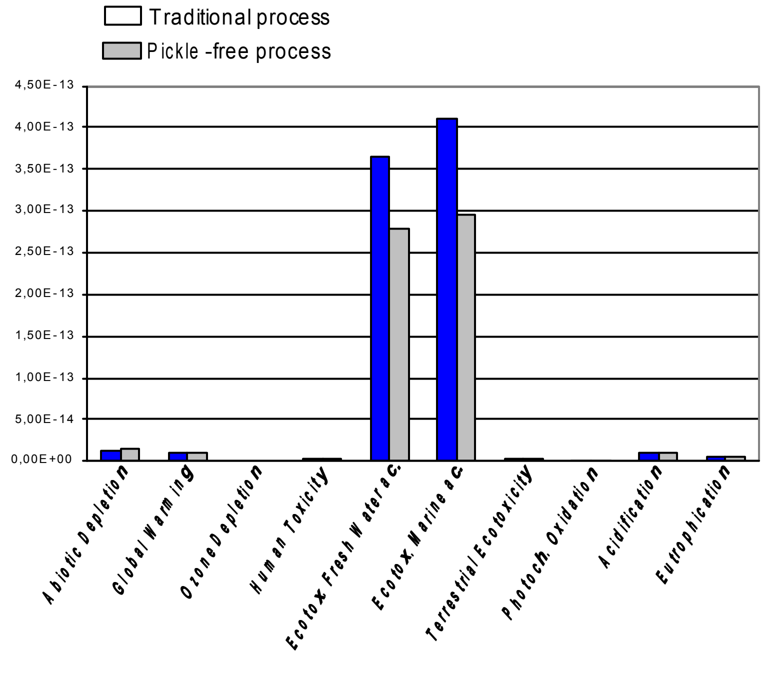


**Fig. 3 Normalized results per impact category**

## 5 Conclusions

In the present study, an innovative chrome tanning procedure based on the use of chrome alum has been assessed on pilot and semi-industrial scale. The crust leathers obtained are comparable to that obtained by the conventional process and are characterized by good mechanical and technical properties.

The innovative pickle-free process is associated with a reduction of the consumption of basic chrome sulphate. Besides, the use of sodium chloride and sulfuric acid is avoided and a significant reduction of chlorides and sulphates dissolved in the exhaust baths is obtained.

The outcomes of the environmental impact assessment showed that the environmental burdens of the tanning process are reduced using the innovative procedure. The results show that "*Fresh water aquatic ecotoxicity*" and "*Marine aquatic ecotoxicity*" are the most affected impact categories and that, damages on both these impact categories are reduced through the adoption of the picke-free tanning process.

Then the results obtained indicate that the pickle-free tanning process is a promising alternative to the conventional process to overcome the ever increasing environmental constraints.