



Green Leather Industry for the Environment (greenLIFE) is a project run by a group of industry partners in Italy's Arzignano tanning cluster. The project partners have committed to sharing their findings by publishing a series of papers in World Leather. The third of six greenLIFE articles comes courtesy of chemical supplier Ikem, one of the project's partners.

greenLIFE 3: New renewable tanning technologies

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1. Introduction

In the last decade, the tanning industry has faced a number of issues relating to the environmental impact of the tanning process and has sought to improve the working conditions of its employees to gain competitiveness in the world market. Legislation is increasingly restrictive, forcing tanneries to continually improve their production activities. Moreover, the competent authorities, together with consumers, are looking more and more carefully at the possible presence of hazardous and noxious substances, such as formaldehyde and hexavalent chromium in leather and in articles made of leather. Wet white leather, which is tanned without the use of chromium salts, can involve the use of multiple tanning substances, including synthetic tannins, vegetable tannins, glutaraldehyde, aluminium salts or zirconium, for example.

The development of the wet white technology is mainly due to the growing demand in the automotive sector for products free of chromium. In fact, since 2000, in all countries of the European Union, Directive 2000/53/EC for the 'disposal of waste from scrapped vehicles (End of Life Vehicles)' has been in force. The directive aims to protect the environment by eliminating or reducing the use of substances known to be hazardous (lead, cadmium, mercury, hexavalent chromium) in the construction of vehicles, and by promoting the collection, reuse and recycling of materials from scrap produced at the vehicles' end of life. By 2015, 95% of the materials that make up a car had to be recycled.

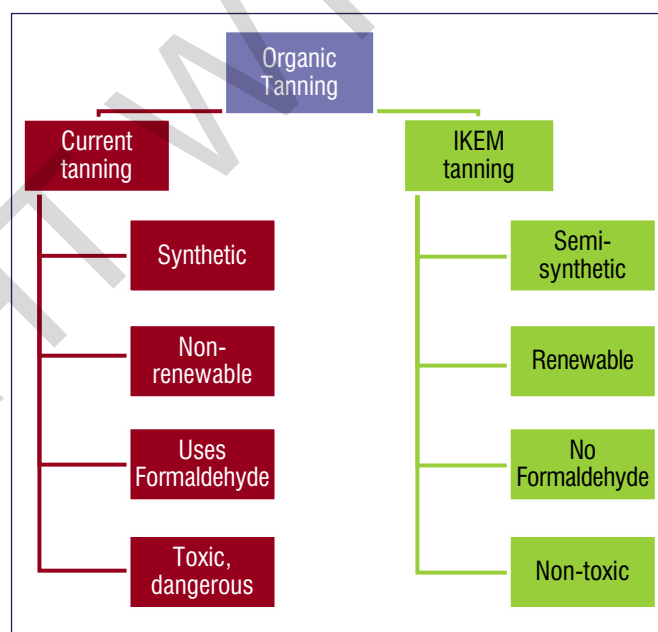
In addition, possible concerns of consumers over the content of hexavalent chromium in leather are greatly accelerating the development of alternative tanning methods.

The goal of our work is to develop a tanning system that is sustainable, competitive, non-toxic and non-polluting, but which is, above all, derived from renewable and readily available resources. To this end, a process has been developed to upgrade by-products, such as polysaccharide, and transform them into tanning products, thereby obtaining a final leather with water and heat resistance and organoleptic properties similar to or better than the organic tanning products currently on the market.

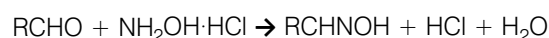
2. Material and methods

Determination of aldehydes in polysaccharides:

The content of aldehyde groups was determined by exploiting the reaction between the aldehydes and



hydroxylamine hydrochloride for the formation of oximes:



Solubilised and oxidised polysaccharides are adjusted to pH 4 with 1M HCl (Hydrochloric Acid). Then, a 0.3M solution of hydroxylamine hydrochloride is stirred into the solution in small instalments, in excess of the estimated value of aldehydes. During the reaction, the pH is kept constant by adding, drop by drop, a solution of 1M NaOH (Sodium Hydroxide) contained in a 50ml burette and monitoring the pH value with a pH meter. After adding the hydroxylamine solution, the reaction must be followed until several decreases in the pH have been observed.

The percentage content of aldehydes, in relation to the glycosidic mole unit of the polysaccharide, was calculated according to the following formula:

$$\text{mol\%-CHO} = ((V_{\text{ml NaOH}} \times M_{\text{NaOH}}) / 1000) / \text{glycosidic mole units} \times 100$$

where $V_{\text{ml NaOH}}$ = ml of NaOH added until the pH stabilises and M_{NaOH} = the molar concentration of Sodium Hydroxide



Determination of aldehydes in final tanned leathers: UNI EN ISO 17226

Determination of aldehydes in final chemical product: UNI EN ISO 27587

2. Results and discussion

Natural polysaccharide was dissolved in water and oxidated for the product to obtain the desired aldehyde functions. The final product presented as a homogeneous solution with a white to yellow colour and a dry content of 27-28%, pH 6.5-7.5.

The content of aldehydes is designed according to the concentration of the oxidant used; for this research, the tests were performed with a content equal to 50% aldehydes.

2.2 Leather tanning procedure

New tanning is developed in a very simple but controlled manner. You can start from soaked or pickled hides; *Table 1* shows an example of a process using soaked hide.

The greater tanning strength of the new product (measurable by the shrinkage temperature, which gives the hydrothermal stability of leather, and its organoleptic appearance) is provided by a pH between 7.5 and 8.5.

The tanning process can take place at an acidic pH, such as that of the solution of the pickled hides, or at a neutral pH, which makes it possible to use soaked hides.

Temperature proves important especially in the final phase of fixing and crosslinking the tanning agent. It was found that a temperature of 35-40°C for approximately two hours of fixation provides the best result on the final tanned hides, in relation to the shrinkage temperature.

Results in the tanned hides:

- Leather is white-yellow in colour.
- Easily pressed and shaved.
- Shrinkage temperature 75-78 °C.
- Simple process
(ability to eliminate pickling)
- High resistance to heat and light
- Good tensile strength and resistance to tearing
- Suitable for many items, especially soft items with a grain

The concentration of the tanning product establishes the magnitude of the tanning action, which is determined by measuring the shrinkage temperature with the IUP 16 method.

Figure 1:

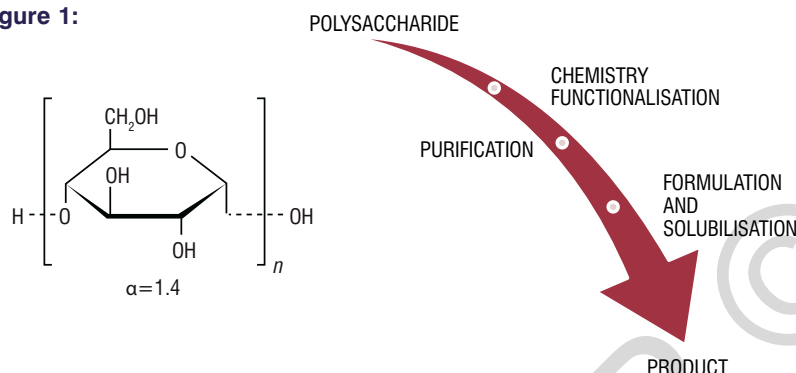


Figure 2: Shrinkage temperature vs concentration of tanning agent to pelt weight

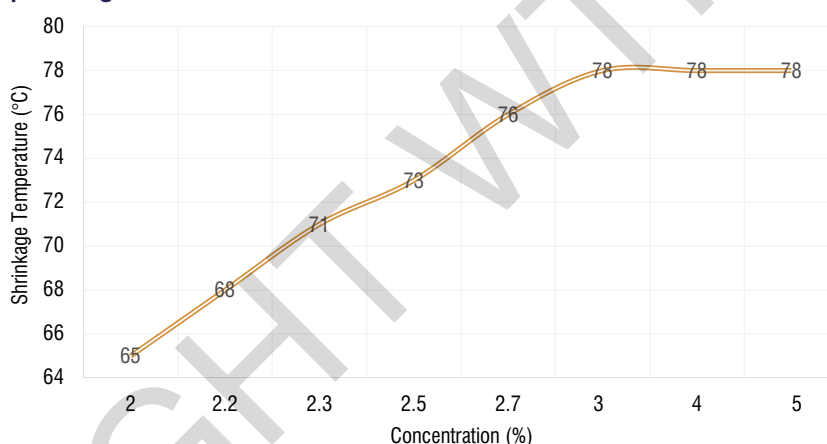


Table 1: Tanning recipe for French bated bull hide 37+

Product	Concentration to pelt weight (%)	Duration	Remarks
Water 25°C	40		
NaCl	6	60'	pH = 8
Deliming Agent	0.2	60'	pH = 6
Tanning Compound	10	3h, 30'	pH = 6.7
Fatliquor	1.5	30'	
Basifying Agent	0.3	60'	pH = 7.5
Basifying Agent	0.3	60'	pH = 8
Run overnight			
Basifying Agent	0.3	60'	pH = 8.5
Wash and drain			

Table 2: Strength and chemical properties of final leather (automotive) – leather thickness of 1.4mm

Property	Testing Standard	New Ikem product	Standard wet white tanned leather
Tensile strength (N)	UNI EN ISO 3376:2006	85 (average)	> 80
Elongation at break (%)	UNI EN ISO 3376:2006	50 (average)	35-60
Tear propagation force (N)	UNI EN ISO 3377-1	25-37	> 25
Chromium content (%)	DIN EN ISO 5398-2	< 0.01	< 0.1
Load tear (N) perpendicular	UNI EN ISO 3377:2008	69	> 60
Formaldehyde content (ppm*)	UNI EN ISO 17226	< 16 for upper leather	< 16

*parts per million



Figure 3: Pressed and shaved finished leather.

The higher the concentration of the tanning agent in relation to the pelt weight, the higher the shrinkage temperature, up to a maximum of 3.5%, considering it at 100% of active substance (Figure 2).

The leather was pressed and after being stacked for 24 hours it was split and shaved to a thickness of 1.4mm. The results of physical tests on the crust are explained in Table 2.

4. Conclusion

A process has been developed to create a new organic tanning product that obtains a finished leather with high mechanical and physical strength and organoleptic properties, similar to or better than the organic tanned leather currently on the market.

The crucial advantages of the new tanning product can be summarised as follows:

- Metal-free and, in particular, chrome-free tanning
- No free or releasable formaldehyde in the finished leather
- Leather with higher biodegradability than those tanned with chrome, vegetable or synthetic tannins or glutaraldehydes (studies not presented in this article)
- Economic and technological competitiveness
- Ecologically and socially sustainable process.

5. Acknowledgements

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