NEW OIL TANNING PROCESS

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ABSTRACT
A new tanning process based on renewable natural oils with specific additives (patented). This new process can be realized by using the common tannery equipment. The new oil tanning can be developed on all type of hides (even on big size); leather may be used to produce all type of items.
Since the materials come from natural origin source, the obtained leather are free from all "undesired" chemicals listed in restrictive MRSL.
If we compare this new process with the traditional old oil tanning, the obtained leather shows an improved technical characteristics, increased dyeability (even on light colour) and very low smell

Keywords: oil tanning, renewable natural source, tanning process, all type of hides

1. Introduction

The last market requests are more and more restrictive on leather chemicals auxiliaries; if we sum-up them, the most recurrent adjective, in new target leather making, is: FREE. The well known Chrome free leather has evolved in Metal free items: any kind of metal cannot be used for leather tanning. Because formaldehyde and other aldehyde get usage restriction, any kind of such substances must not be present on leather, including all chemicals that release aldehyde (such as oxazolidines). In the very last period, also Bisphenols are not welcome. In addition, not only leather material is focused by the new requests but also the chemicals used in tannery: the growing demand to avoid use of SVHC chemicals reduces again the potential process of making leather. Moreover, a greater biodegradability of leather materials is appreciate by the end-user. The current processes that may give an answer to all these requests are two: Vegetable extract tanning and oil tanning. About vegetable tanning, many items and processes are developed: this technique is widely diffuse for leather making. On the contrary of vegetable tanning, oil tanning process is not a widespread use for producing leather: due to its particular criticism and items, very few tannery produce this kind of material. It was our idea to investigate this old tanning technique to improve it and get the answer to the modern requests.

2. Materials and Methods

The hides used to develop the new process and run all tests are sheepskins and big cattle. By using sheepskins it is possible to compare the new oil tanning process with the traditional ones; with the big cattle hides (bull butt, shoulder and similar) it is possible to dimoster the efficency of the new tanning process on any kind of raw hides. All applicative test are carried-out in Sani&Testai Stainless Steel Drum model ST950.

To identify tanning degree, determination of shrinkage temperature is runned by using UNI EN ISO 3380 method with Automatic Leather Shrinkage (TG/GT) modified Giuliani Theiss equipment.

Infra Red Analysis are carried-out by using FTIR equipment from Perkin Elmer, model Spectrum 100. Poly-unsaturated vegetable oils are used as tanning materials.

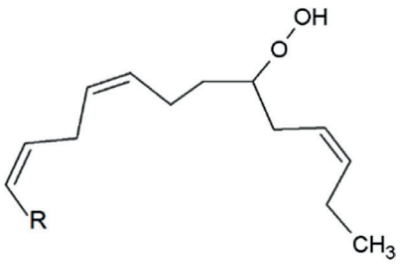
3. Results and discussion

In the traditional ancient tanning process, the main and typical steps are basically 3:

- 1. on a pickled pelt, a strong mechanical action is required to diffuse the oil matter in the hide fiber structure (usually this process is made in stocks hammer or dry drumming);
- 2. oxidation of oils by air blowing in appropriate drum or room (oxidation is runned with hot air);
- 3. removing of oxidized excess oil by using organic solvent (the by-product of this processes is the well known "degras").

During the oxidation step the actual tanning takes place between the oils and proteins. The tanning mechanism is quite complicate because the oils oxidising reaction gives rise to several products that participate together to proteins modification. First of all the reaction between triglycerides and oxygen produce an hydroperoxy group (Fig.1) on the conjugated poly-insatured carbon chain of the fish oil (oil commonly used in this tanning type)

Fig.1



The hydroperoxy group may follow, basically, three different pathway:

- Make a direct reaction with the protein group and fix on it,
- Make a reaction with other hydroperoxy groups and produce an oil polymerization,
- Undergoing an hydrothermal and oxidative cleavage, create several types of aldehyde.

All these pathways give an interaction with proteins or pelt fiber structures and produce the common items well known as "chamois".

This traditional oil tanning process has several issues. To running the tannage, a fish oil must be use that, thanks to its hight auto-oxidative properties, can guarantee the tanning effect; the oils are not a renewable materials and the continuos marine resource reduction let them not to be an environmentally friendly stuffs. In addition, it is difficult to reach a proper oil diffusion on big hide; during the treatment the pelts are permeated of water (40% approx. on total pelt weight) that avoids the good compatibiliy between oil and protein fiber: for this reason the oil tanning process is commonly made on sheepskin splits that can easily absorb the oil in theire spongy structure (in the past, small deer hide was used). For same reason, specific machine are required (stocks faller or dry- drumming) to guarantee oils diffusion. Moreover, the aldheyde formation during oxidation process produces an unpleasant smell and light brown colour of the finished items. The high amount of oil used during tanning process (approx 40% on leather weight) increases cost and pollution; normally, only 15% of oils total quantity is fixed on leather fibers.

To solve the mentioned problems, FGL International developed a new patented oil tanning process that improves various aspects of the old traditional ones.

First of all, we introduce an appropriate tensioactive that promotes a better penetration of oil matter in a damp pelt. The improved oils diffusion in protein structure imparts wide benefits:

- Reduction of mechanical action: the tanning process can be conduced in normal tanning drums, any tannery may produce this kind of items.

- Possibility to work on big hides: the water inside pelt, instead of resisting oils permeation, becomes a carrier that helps the diffusion of tanning material across the section even on thick hide as bull butt, shoulder or similar.
- Oils amount reduction: the improved affinity between oil matter and proteic wet fiber guarantees a deeply diffusion of oils inside interfibrillar structure and allows to use the strict necessary amount of oils to reach the properly tanning effect (12% instead of 40%); treated pelts show low oily touch on their surface at the end of drumming step.

On the other hand, the addition of an appropriate organic catalyst (heavy metal free) improves the oxidizing reaction of oil; the boostered oxidation imparts wide benefits:

- Possibility to use vegetable oils: no need to use very strong auto-oxidative oils (such as fish oils) to run the tanning process; the potential use of renewable sources for oils production reduces the environmental impact of the process.
- Possibility to work on big hide: the strong radical oxidizing reaction run across the section and fix the oil matter even on thick hide as bull butt, shoulder or similar; gelatinization temperature of thick treated leathers is the same as the thin ones, the section of heavy leathers looks uniforme, tanned and lubricate as the small ones.
- Lower aldehydes formation: during the oxidizing step, very low aldehydes smell is sensed and very light coloured leather is produced; tanned leathers with the new process show similar gelatinization temperature of the traditional ones (68°C approx.): increased tg proves the success of the process. The successful fixation of the tanning substance in the protein structure is also demonstrated by the FTIR spectra analysis. The IR traces of the leather, after the tanning treatment, show an absorption signal in the frequency of the triglyceride carbonyl group combined with the reduction of the amino group absorption signal; this shows that the free amino groups of collagen interact with the oxidized oil which remains firmly attached to the protein even after vigorous degreasing with organic solvents. In addition, there is no presence of peroxide groups in the tanned material.

To optimise the process and improve item steadiness, it's better to run a pre-tanning treatment. In the traditional oil tanning process, pre-tanning step is carry out with glutaraldehyde. Since our target is to reach good tanned leather without any chemicals material listed in stakeholders MSRL, a very low amount of vegetable extract is added: from 4% to 6% on pelt weight. It's also possible to process the pre-tanning step by using a small amount of replacement phenol syntans (low bisphenol content type), finished items will show a very light colour; total amount of bisphenol free on leather will be much less than the more restrictive market request. Moreover, is registered an increased gelatinization temperature on finished leather with pre-tanning phase (about 70°C) even if the pre-treated pelts tg it's similar to not pre-tanned ones (53°C). We suppose that a synergy interaction by the different tanning materials may improve the proteins stabilization.

Pre-tanning phase is also indispensable to get a correct shaving; shaved pelts are much easy to treat in oil tanning process. In addition, the total weight of pelts to be treated in tanning process is less if compared to unshaved ones: a reduction of oil demand and cost is registered on this uniformized materials.

Finished items, resulting from shaved pelt, looks uniform, round, softly and with pleasant touch.

Here below the recipe description of the whole process starting from pickled pelt to finished item.

MATERIAL: FROM PICKEL PHASE		***THIKNESS: FULL***	
%	*Products*	*Run*	*Check*
	MORNING	10'	pH 3,8
+			
6,0	VEGETABLE EXTRACT	4h	SECTION ≠
+			
0,8	SODIUM BICARBONATE	90'	
1	SODIUM FORMATE		pH 5,5 - SECTION ≠
	DRAIN		

	SETTING OUT		
	SHAVING		
	% ON SHAVED WEIGHT		
12	VEGETABLE OILS BLEND	4h	
2	TENSIOACTIVE		SECTION ≠
+			
0,5	CATALYST	O/N	INCREASED TEMPERATURE
	MORNING		ABSORPTION
	UNLOAD		
	HANG TO DRY	24h	45°C
	DRY WASHING	40'	
	DRYING	60’	
	UNLOAD		

4. Conclusion

The developed oil tanning process let possible to treat various types of hide (even if big one) with natural origin products that are free from “unwanted” substances listed in MSRL requests.

If the new tanning process is compared to the ancient fish oil treatment, the items characteristics are significantly improved: the leathers, at the end of the process, have a light colour and an increased dyeability, has also round touch and look with very uniform appearance; furthermore, items olfactory impact is zero or, at most, barely perceptible.

In addition, there is no need for the tannery to modify theirs equipment and machinery: the oil diffusion is guaranteed by the use of chemical additives with dispersing effect while the oxidation phase is boostered by the selected catalysts which guarantee an effective tanning action.

Thanks to the use of vegetable oils (renewable sources) and a technologically improved process, it is possible to obtain a leather that meets actual requests and, at the same time, produces more environmentally friendly and more healthy material for tanning operators and end-users.

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Note