FROM SKIN TO LEATHER
IN DENSE PRESSURIZED CO_2

C. Perre[(1)] – A-L Hans[(2)] – M. Dedieu[(3)] – O. Gand[(4)] – L. Saldinari[(5)] – L. Dutel[(6)]
[(1)] CEA VRH – DEN/DTE/SLP – BP111 – 26700 PIERRELATTE (France)
e-mail : christian.perre@cea.fr - fax : 33 404 7550 4342
[(2)]CTC- [(3)]IFTH - [(4)]ITECH - [(5)]Tanneries ROUX - [(6)]ATC co.

Introduction

Ancestral gesture improved all along, the transformation of skins into leathers includes several stages with a complex aqueous chemistry.
The main stages are: *Raw hide* = > **Beamhouse processing** = > *Pelt* = > degreasing / Pickling = > Pickled skin = > **Tanning** = > *Wet blue, Wet white*_= > **Dressing** (retanning+ dyeing + fat liquoring+ drying+ staking, etc..) = > *Semi-finished leather* = > **Finishing** = > *Leather.*
In order to perform efficiently all these stages, the pH of the aqueous solutions should be well tuned. As a matter of fact, the acid functions of collagen (- COO^-) are active if the pH is greater than 5.5 (iso-electric point of skin), and in opposite, the basic functions appear (- NH3+, - NH2+) for the lower values.
Large amounts of water are necessary to perform all these transformations that are generating important volumes of effluents and sludges, whose treatments and storages are more and more controlled.

The main goal of this work is to replace this traditional medium by dense CO_2, which generate almost no pollution.
A first study was successfully carried out on the skin degreasing by dense CO_2 with half sheepskins.
Tanning with chromium salts or vegetable extracts were also carried out on whole sheepskins.
All these stages, and dyeing also, are achieved at the pre-industrial size.
The first chemical state of the skin and the used compounds were adapted at each stage.

I - Which are the possible stages in CO2 medium ?

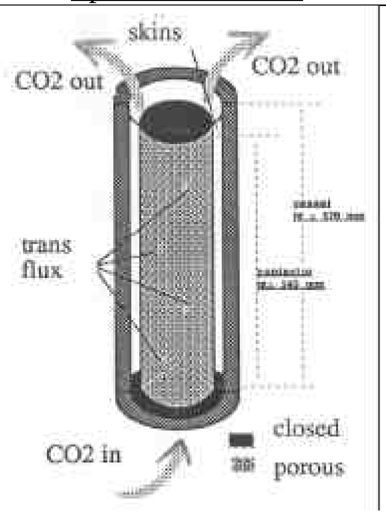
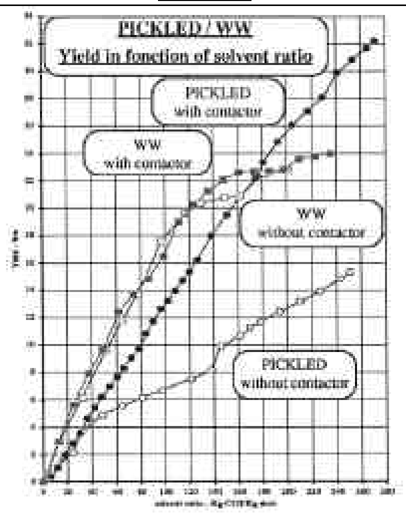
The study of the Sichuan University, (People Rep. China – 1999) [1] show that several stages are possible in supercritical CO_2.
On a small size apparatus, Liao Longli and all have carried out the following stages :
- degreasing : at 9.3MPa, 37°C, 2.5 h,
- dyeing with or without additives : at 9.5MPa, 36°C, and with 2% of acid black,
- protein enzyme dehairing : at 9.3MPa, 37°C, 2 or 4 h and with 166 or 1398 enzymes plus additives,
- deliming : at 8.5MPa, 37°C, 0.75 h,
- chrome tanning : at 9.0MPa, 41°C, 2 h and with 5% KMC and 10% additives,
- vegetable tanning : at 9.3MPa, 37°C, 6 h and with 25% pine tree extract, 25% red bayberry extract and 10% additives,
- dyeing and fat liquoring : at 9.0MPa, 37°C, 1 h and with 1% acid black, 18% multiple function anionic fat liquor and 5% additives.

II - Degreasing sheepskins process by SC CO_2.

This research has been carried out in collaboration between CEA and Leather Technology Center (Centre Technique du Cuir -CTC) at Lyon (France) [2]. The aim was to study the degreasing of sheepskins by supercritical CO_2 extraction.
Two different types of skins have been treated : Pickled and wet white (WW).
On the WW type, the extraction rate is faster than the pickled skin, and the maximum of fat extractible part is .55%, more than with the present process : 46%.
On the pickled skin, the degreasing ratio is 67% compare to 80% with the present process. But it is possible to have greater degreasing ratio with a greater solvent ratio.
The quality of treated skins is good and the skins stay dry.
To operate efficiently in the porous structure, the minimum density of CO_2 required is 0.85 Kg per dm3 and 40°C seems to be the minimum temperature for diffusion mechanisms.
Several tests have been carried out. Results are reported on table 1.

1st. series – without contactor – loading in thigh rolls						
Type of skin	P	T	Skin weight	% variations		
	bar	°C	g	Weight	H2O	fats
PICKLED	300	40	1240	-20.5	-16.9	-41.2
WW	300	60	1540	-29.2	-21.4	-25.7
2nd series –loading on special porous contactor						
Type of skin	P	T	Skin weight	% variations		
	bar	°C	g	Weight	H2O	fats
PICKLED	300	40	1660	-38.5	-30.6	-66.7
WW	300	60	1617	-26.9	-11.9	-55.5
Present process – white spirit						
Type of skin				% variations		
				Weight	H2O	fats
PICKLED					18.3	-81.1
WW					11.9	-46.2

A specific contactor in porous stainless steel is more efficiency (see below fig.1).

Specific contactor	Results
	

III - Wet skin tanning with chromium in dense pressurised CO_2

Making leather from hides, a time perfected tribal skill, comprises several stages the main one is tanning. The aim of this process is to make the hides imputrescible or rot proof and increase their mechanical properties. Today, 90 % of world leather production is tanned using chromium.

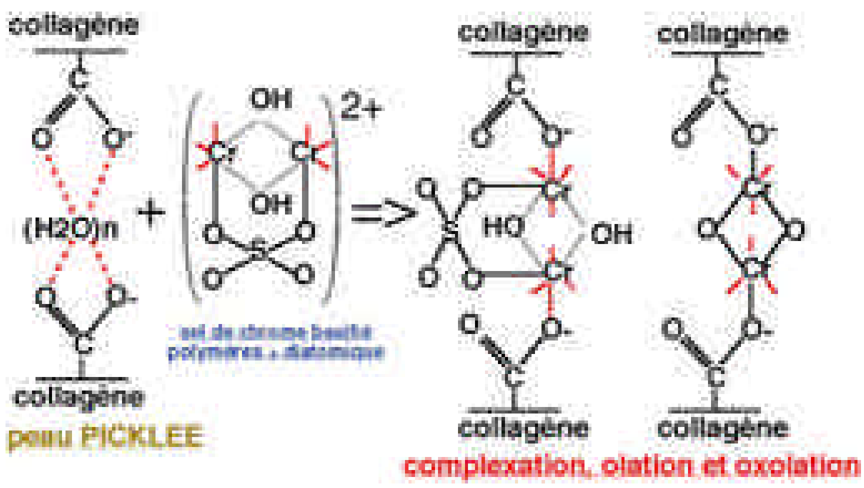
However, in chromium tanning (Cr III), about 700 litres of water per metric ton of hides are required for this single operation. To reduce the volume and the chromium content of the effluent and sludges produced, therefore becomes a major issue.

The present study was carried out in collaboration with three tanning companies of the Rhône-Alpes-Auvergne area (France) and a manufacturer of tanning products (ATC).[3]

The difficulty of this study relies in the chemically opposed character of the two involved media. CO_2 is a non-polar and lipophilic solvent in which mineral salt of chromium is insoluble. The water, contained in the treated skin, is a polar and ionic reactional medium and one of the reagents of the tanning chemistry. The mixture of CO_2 and water, partially miscible compounds, gives a pH equal due to 3 by carbonic acid formation.

Chromium salts are the most important family of tanning agents. According to the WERNER theory of complex salts, chromium (III) has a coordination number of 6. This means that the formation of hydroxylated polyatomic compounds can be predicted. The tanning process depends on the average size of the diatomic compounds in relation to the interfibre space of the collagen. (see fig. 2 under).

Figure 2 : Diagram to show the chromium tanning reaction of di-atomic compounds



To introduce CO_2 into the transformation process, the hides were tanned at the pickling stage and the water was conserved as a reagent of the tanning process. The chromium salts were suspended in CO_2.

The process was carried out in a 10 litres cylindrical autoclave, equipped internally with a horizontally rotating basket. This apparatus is close in conception to a traditional milling machine. Then we made a validation on the industrial apparatus of 100 litres of volume and entire skin. (see fig. 3 under).

10 litres vessel with rotating basket.

Industrial apparatus – 100 litres

The optimum conditions were found to be: 80 bars, 37 °C, 15 to 20 minutes saturation time and 2 hours for neutralisation. The chromium sulphate was a modified salt (powder less hydrophilic — ACTAN series belonging to the ATC company), and, the basic chemicals were ACTIPLEX CPS (ATC Co.) associated with sodium bicarbonate.

The results obtained compared to the traditional aqueous process are reported in table 2 below; the objectives were achieved.

Table 2 : Comparison of the two tanning methods.

	Chrome tanning in aqueous medium	Chrome tanning in pressurised CO_2	Comment
Initial amount of Cr_2O_3 (kg/T raw hide)	**12.5 - 35**	**8**	Reduction in the initial quantity of chromium
Volume of water (litre/T raw hide)	**700 - 800**	**0**	No aqueous waste
Tanning time (in hours)	**6 - 8**	**2 - 3**	Reduction in time
Cr_2O_3 in the half finished leather (g/100 g dry leather)	**4.5 - 5.5**	**3.8**	Lower chromium content but better distribution
Cr_2O_3 waste (kg/T raw hide)	**3.5 - 18.5**	**0.4**	Lower chromium content of total effluents produced (10 - 45 times less)
Fixation performance (fixed q^{ty} Cr_2O_3 / initial q^{ty} Cr_2O_3)	**45 -72**	**95**	Clear improvement in fixation performance.
Shrinking temperature (°C)	**100°C**	**108°C**	Comparable physio-mecanic properties.
Tearing strength (daN/mm)	**>5 (full thickness) >1.7 (split to 7/10)**	**7.3**	
Organoleptic Quality		**High quality Comparable suppleness**	Satisfying quality

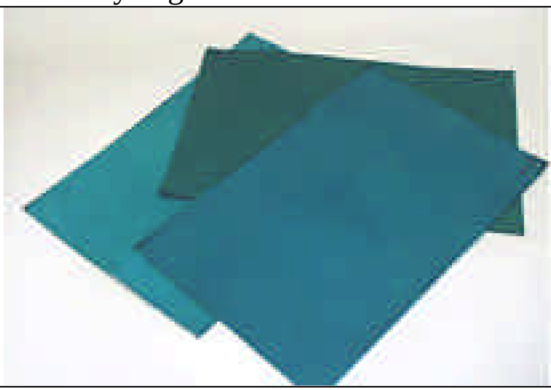
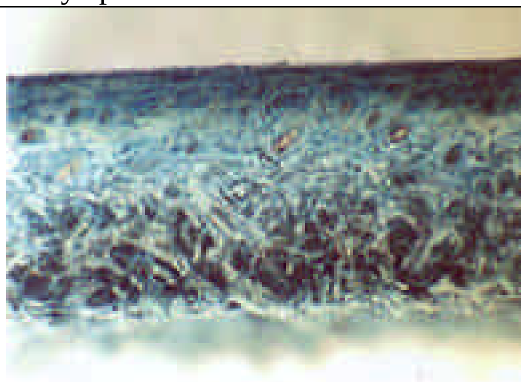
What is the role of CO_2 in the process ?
To answer this question, indirectly tests were carried out in air at atmospheric pressure (dry tanning) and in nitrogen at a pressure of 150 bars.

They gave very different and unsatisfactory results : uneven stratigraphic distribution of the chromium or of the final colour hence a different chemical compound form, and, lover Shrinking temperature.
CO_2, and its affinity to water, plays an important role in the saturation and fixing of chrome.

IV – Dyeing of leather in SC CO_2 medium

This research, financed by the Rhône-Alpes Region has been carried out in collaboration between CEA, CTC (Leather Technology Center) and IFTH (Textiles French Institute). The aim was to study the dyeing of leather in supercritical CO_2 medium.

The trials have been made with several different dyes and additives leading to the choice of a single dye and additive. The corresponding dyeing conditions have then been optimized at lab-scale. Finally, six samples of "A4" size, with 3 different types of leather, have been treated within a single trial in an industrial apparatus of 100 liters.
The pilot trail seams promising has it led a uniform dyeing, with a relative good dye penetration. Among the advantages of this dyeing method, the dimensional stability of the treated leather can be mentioned.

Uniform dyeing of the leathers:	Good dye penetration:
	

Conclusion

It is possible to transform skins into leather in supercritical CO_2 medium.

We have shown this about 3 stages at the industrial scale : degreasing, chromium tanning and dyeing, using a 100 litres apparatus able to treat some whole hides.

However, this new process is a major industrial change with high investment. Therefore, industrial application will be possible only if most of these stages of transformation are carried out in the same apparatus.

References

[1] " Study on non-polluting leather making technology, using CO_2 supercritical fluids. Feasibility study on CO_2 supercritical fluids clean production technology of leather"
Liao, Longli ; Feng, Yuchuan ; Chen, Min ; Li, Zhiqiang.
Protein Laboratory, Dept. Of Leather Engineering, Sichuan University, Chengdu, 610065 People Rep. China Zhongguo Pige (1999), 28(9), 14-16, 25
CODEN : ZHPIEL ; ISSN : 1001-6813

[2] Patent n° F92/11703 extended to PCT FR93/00960

[3] Patent n° 99/13589