Fast Chrome Tanning by Immersion of BCD

Dr. José María Adzet[1], Silvia Sorolla[1], Joan Carles Castell[1] and AIICA Technical Team

[1]**AIICA:** Association of research of leather industry and annexes. IGUALADA. Spain.

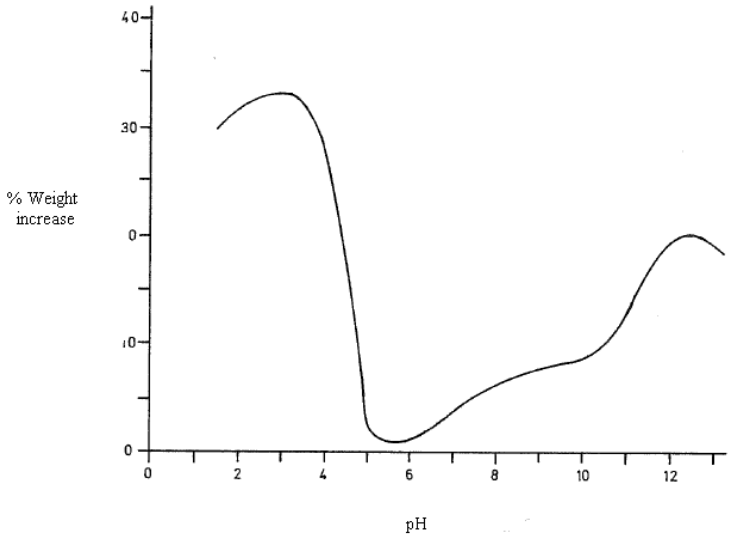
Abstract: A material based on dehydrated collagen from hides and skins has been industrially developed. Its spongy properties allow an instantaneous and continuous chrome tanning process with considerable saving in time and chemicals.

Key words: instantaneous chrome tanning, immersion, dehydrated collagen.

1.- Introduction

The aim of this work is to develop a new instantaneous chrome tanning technology by immersion of one specific type of dry pelt that we call "BCD" (Biomaterial collagenic dry) in a solution of basic chrome salt. We obtain a very fast penetration of the chrome salts solution through out the weave fibres from hides an skins. The BCD material has the fibres separated and absorbs the solution likely a sponge. This new tanning process reduces drastically the amount of pollution.

The fibers of the wet pelt contain more or less amount of water according to its pH. The isoelectric point of the limed pelt is at pH 5.2. At this pH fibers contain less water. The following chart represents the swelling of the pelt at different pH values.



Swelling graphic of pelt at different Ph

2.- Experimental section

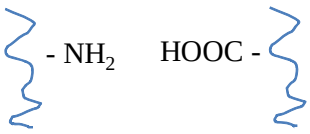
If we dry a delimed and bated pelt we obtain a translucent and corny material. During the drying operation, the fibres are linked among them becoming a translucent material hard and compact that is difficult to be penetrated by a solution.

Fibres in aqueous medium ***Dry fibres***

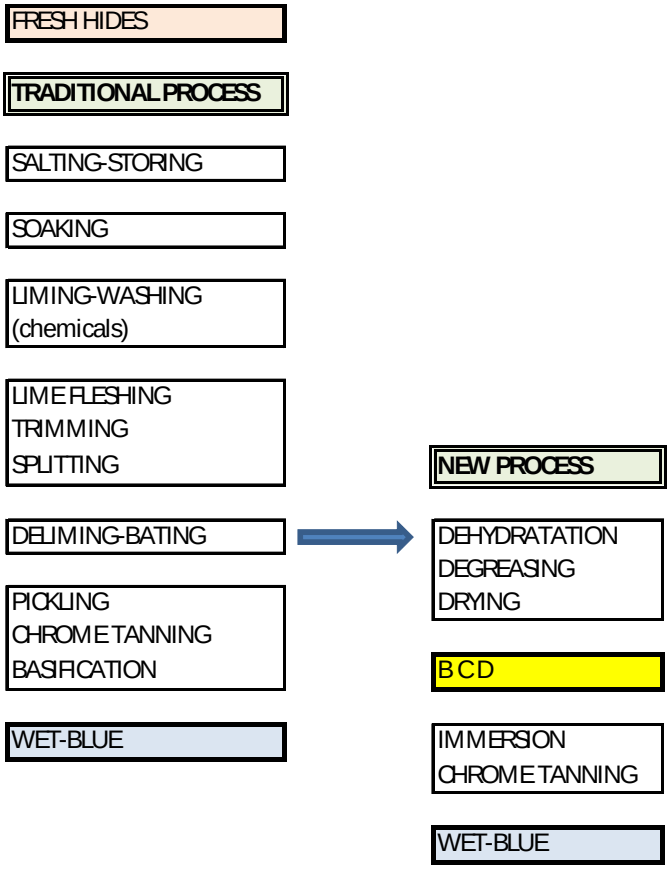
If we are willing to obtain a spongy flexible and opaque material that can absorb a solution, we must be aware that the fibres remains separated during the drying process. One way is to change the medium polarity of fibres from water by an organic solvent (ie. Acetone which is less polar).

Solvents	*Boiling point*	*Dielectric constant*	*Latent evaporation heat*
Water	100,0ºC	80,1	2257 Kjoule /Kg
Acetone	56,0ºC	21,1	501 Kjoule /Kg

To eliminate all water content from a bated pelt , we must begin by samming it, and follow we shall make three washings with pure acetone. By reducing the immersion medium polarity the ionic groups of fibres are discharged . If later the acetone is removed, the reactive groups have not the electric charge and during the drying operation they can not link one to another, the fibres remains separated and we will obtain a fibrous pelt, flexible, opaque, spongy and white.



Separated dry fibres



The bated pelt are adjusted to pH 5, mechanically sammed and introduced into the dry cleaning equipment. Alternation of acetone washing and centrifugation reduce the water contain. At the end of few cycles, the pelt is completely dehydrated and the bath drained. By heating, the solvent evaporates easily and by cooling is recovered to be used in further washings. Finally, pelts are completely dried and dehydrated obtaining, BCD (Biomaterial, Collagenic, Dehydrated).

By this process, grease is removed at the same time than the water. This is a very important fact, especially when treating fatty pelts from sheep skins. Thus, dehydration and degreasing process are free of surfactants. Separation of grease and water is technically plausible too, at a very low cost with the possibility to recovered the grease.

One of the problems to obtain a new "BCD" material , appear when we remove the acetone from the impregnated pelt . One possibility is to evaporate the acetone in the ambience air. With this operation there are two inconveniences:

- the acetone mixing with air can be explosive.
- The evaporation of acetone produce cool and the existing water vapour in the ambience can condense on the "BCD" surface material.

On wetting the fibre the reactive groups are ionizated and dry as corny spots.
The water condensation of ambience is similar to what occurs in summer when the ambience water vapour condense in the external side of a glass that contains a cool drink.

In the table 1 we give some values of the new "BCD" material comparatively with "vachette" (vegetable tannage) and a garment leather (chrome tannage) to make them more comprehensive.

3.- Results

Table I.- Characterization of BCD and two other leathers

Physical and fastness-related performances	Units	BCD Pelt	Vachette (vegetal)	Garments leather (chrome)
Tickness IUP-4	mm	2,05	3,04	0,88
Tensile strength and elongation IUP-6				
Strength	N/mm^2	35,5	29,7	11,2
Elongation	%	47,5	44,7	44,3
Static water absorption (Kubelka) IUP-7				
After 1h	%	106,1	55,9	142,6
After 24 h	%	123,3	61,1	164,8
Tear resistance IUP-8				
Strength	N/mm	65,9	131,6	31,8
Measurement of distension and strength of grain by the ball burst test IUP-9				
Grain layer crack				
Thickness	mm	2,06	3,02	0,86
Strenght	Kg	58,3	125,9	22,1
Distention	mm	9,3	9,5	9,4
Leather crack				
Strenght	Kg	112,4	137,5	28,7
Distention	mm	12,2	10,2	11,1
Water penetration (waterproofing) IUP-10				
Total time		1h	1h	1h
Penetration time	%	4'30"	48"	1'27"
Water absortion		97,6	60	233,7
Throught out water	g H_2O	0,7	1,8	3,7
Water vapor permeability IUP-15				
Water	mg/cm^2 h	8,1	3,9	5,7
Srinkage temperature IUP-16				
Temperature	ºC	54	77	118
Bending resistance IUP-20				
100.000 flex		without cracks	without cracks	without cracks
Light fastness IUP-402				
	Blues scale	> 7	1	6
Colour fastness to water drop IUF-420				
Penetration time		> 30"	1'03"	12'50"
Before manual treatment	Grey scale	1	1	3-4

LEATHER BEHAVIOUR TO IGNITION FOR INSIDE MATERIALS			
Ignition distance (mm)	0 (1)	0 (2)	0 (3)
Ignition time (s)	0.0 (1)	0.0 (2)	0.0 (3)
Ignition speed (mm/min)	0.0 (1)	0.0 (2)	0.0 (3)
Flame testing in laboratoire (with Bunsen burner)	Ignite less that the chrome leather, less smoke and smaller shrinkage, similar to vegetable leather	Ignite less that the chrome leather less smoke and smaller shrinkage	Ignite more than the other, more smoke it's twisted

(1)(2) At take back of the flame from the specimen, after 15 seconds of application, there are not flames Material grading: DNI (Doesn't ignite).
(3) At take back of the flame from the specimen, after 15 seconds of application, there are not flames, but we found ignition points during 120 seconds. Material grading: DNI (Doesn't ignite).
(4) Test not standardized, tested in laboratory we put the leather on the Bunsen flame at a distance of 20 mm. during 30 seconds.

Extractable matters with dichloromethane IUC-4		%	0,07	5,0	8,2
Volatil matter IUC-5		%	14,7	12,3	11,2
Washabel matters	**IUC-6**				
Mineral		%	1,6	1,7	0,8
Organic		%	0,3	2,5	0,4
Insoluble ash IUC-7		%	0,9	1,6	6,2
Chrome oxide IUC-8		% Cr_2O_3	(LD <0,004)	(LD <0,004)	2,76
Total nitrogen	**IUC-10**	% N	18	10,8	13
Hide substance		% collagen	100,9	60,9	73,2
pH measurements	**IUC-11**				
pH			5,4	4,9	4,7
Shrinkage of pelt with 12 % moisture (DSC)		ºC	103,3	123,3	124,7
Shrinkage of pelt dryed at 102 ºC (DSC)		ºC	149,4	159,3	168,4

4.- Discussion

The tanning operation is carried out by immersion of the "BCD" material in a solution of basic chrome salts. The chrome solution goes through in the pelt in a very short time of few minutes. It is something like when a dry sponge is introduced into water it absorbs the water instantaneously. We think that this process has an economic interest, so we have applied for a patent.

The fast absorption takes place by capillarity phenomenon through the free spaces among fibres. Once the solution goes through the "BCD" material the shrinkage temperature becomes higher than 100ºC in less than one hour. The shrinkage temperature of tanned "BCD" depends of the chrome salt concentration, its basicity and the pelt basicity as well. We understand for pelt basicity the amount of acid or base that it contains at the moment of solvent dehydration process.

To fix the chrome salt on the pelt reactive groups, takes part from one side the chrome salt basicity and the other one the pelt basicity.

In the first trial made with dry sheep skins bated at pH 8, dehydrated-degreased with acetone, we carried out the tanning operation by immersion with a solution of 20% of chrome salts and basicity 33%. We were happy with the results, because the shrinkage temperature of the dry chrome skin was of 114ºC what represents a very good stabilisation of pelt weave.

The chrome tanning for bovine hides, using the new technology, must last less than 30 minutes if the temperature of chrome salt solution is between 15-20ºC. That is, the necessary time to carry out the immersion process and to determine the shrinkage temperature.
The stabilisation time for sheep skins is shorter.

However if the chrome salt solution temperature is around 4ºC or lower, the absorption process follows likely fast, but the pelt tanning process slows down. Its duration could be around 3 hours.

This material presents the capacity to react with carboxylic groups of collagen. The solution of 10% chrome sulphate of 33% basicity in cationic form has a pH between 2,8-3,5.

Really, the solution of basic chrome sulphate contain a lot of particles of different sizes with a positive charge, more or less colloidal size, which are the ones that reacts with the reactive groups of collagen.

It is evident that the reactive groups of the dry collagen are not capable to react with aggregates of basic chrome sulphate solution. To do possible the reaction it is necessary to wet the fibres which could be carried out with the water provided by basic chrome salts solution. Once the fibres are wetted the carboxyl groups are negatively charged, they attract electro-statically the basic salt chrome aggregates positively charged and takes place the tanning reaction.
During the absorption process of chromium salt solution by "BCD", the sodium sulphate that contains the solution, it can act as osmotic pressure avoiding the swelling of the fibres due to the solution acidity and facilitates the solution penetration.

The increase of shrinkage temperature from wet blue will depend of the pelt basicity, because the dehydrated-degreased pelt process may be carried out by acid, neutral or basic medium. The fixation of chrome salt to the hide depends of both, basicity from the hide and the salt chrome as well.

5.- Conclusions.

The new technology consists in the preparation of "BCD" dry material from dehydrated-degreased bated pelt . The dry "BCD" is a spongy fibrous material with a very high absorption capacity, which is 100% pure collagen, because it contents of solvent is evaporated during the drying process.

During the dehydration process the pelt becomes degreased, this fact is important for sheep skins because it lets to avoid the degreasing process in beamhouse, also the recovered grease is free of surfactants.

The instantaneous chrome tanning is carried out by immersion of the "BCD" material into a basic chrome salt solution, which penetrates through the material in a very short time.

Applying this new methodology we simplify the degreasing, we avoid the waste bath of pickle, and the tanning waste bath can be reused and we avoid the basification of the chrome tanning .
The final pH is regulated adjusting the pH of the pelt before dehydration. On the other hand it is possible to save the energy necessary to run the drum with pelts and baths.

6.- References

1.- The chemistry and Technology of Leather
Volumen I Preparation for tannage
F. O' Flaherty y otros
Reinhold Publishing Corporation New York 1956

2.- Beobachtungen bei der Aceton entwasserung und der Gefriertrocknung von Hautkollagen
E. Heidemann y W. Riess
Das Leder 14 87 (1963)

3.- Dehydration by organic solvents
Reig G. Kollagen, Steinkopf, Leipzig (1967)

4.- Einfaches Verfahren zur Konservierung eines Standard-Ledersubstrates für Fettungs und Ausfärbeversuche durch Entwässerung mit Aceton
R. Leberfinger und A. Draeger
Das Leder 23 220 (1972)

5.- Maire M. S.
JALCA 71 438 (1976)

6.- Method for the preparation of leather and fur skins
Hans Dieter
Patent US 4039281 (1976)

7.- Process for solvent drying Leather
US Pat. 4.147511
PL Barlett Wilmington 30 junio 1978 via JALCA 75 138 (1980)

8.- Physical, Chemistry of Leather Making
K. Bienkiewicz, R. E. Krieger
Publishing Company Florida (1983)