Dry Biomaterial Production from Fresh Hides and Skins*

by

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Abstract

Fresh hides and skins were processed directly from the slaughterhouse. New unhairing and dewooling operations based on bath temperature control were applied, without affecting the quality and properties of the not yet stabilized collagen fibbers. The objective was the activation of the enzymes already present in raw hides and skins, resulting in an ecological process that avoids chemicals. Only small additions of auxiliaries to control pH were added to the unhairing or dewooling bath. Once hair and wool were removed from the grain side, the pelts were subjected to a solvent dehydration-degreasing operation, where the putrescible collagen material was converted into a stable dry collagen material able to be commercialized and easily stabilized by immersion procedures. It included the design of a new machine to obtain a collagen-dehydrated biomaterial (BCD) in a non-emission cycle using a polar solvent. The results are; curing and soaking are not necessary, salts and sulphides can be avoided. For this reason, this is projected to be a new non-pollutant beamhouse procedure followed by the production of dry collagenic material that is stable, spongy and with no special requirements for their storage and commercialization.

Resumen

Cueros y pieles frescos fueron procesados directamente desde el matadero. Una nueva operación de depilado y deslanado basadas en el control de temperatura del baño se ha aplicado, sin afectar la calidad y propiedades de las aún no estabilizadas fibras de colágeno. El objetivo fue la activación de las enzimas ya presentes en los cueros y pieles en bruto, resultando en un proceso ecológico que evita productos químicos. Sólo pequeñas adiciones de auxiliares para controlar el se agregaron al baño de depilado o deslanado. Una vez que el pelo y la lana fueron retirados de la flor, las pieles fueron sometidas a una operación de deshidratación-desengrasado con disolvente, donde se convirtió el material de colágeno putrescible en un material de colágeno seco estable, capaz de ser comercializado y fácilmente estabilizado por los procedimientos de inmersión. Se incluyó el diseño de una nueva máquina para obtener un biomaterial colagénico deshidratado (BCD) en un ciclo de no emisión utilizando un disolvente polar.Los resultados son: la conservación y el remojo ya no son necesarios, sales y sulfuros podrían ser evitados. Por esta razón, se prevé que este sea un nuevo procedimiento de ribera no contaminante seguida por la producción de material colagénico seco que se mantiene estable, esponjoso y sin requisitos especiales para su almacenamiento y comercialización.

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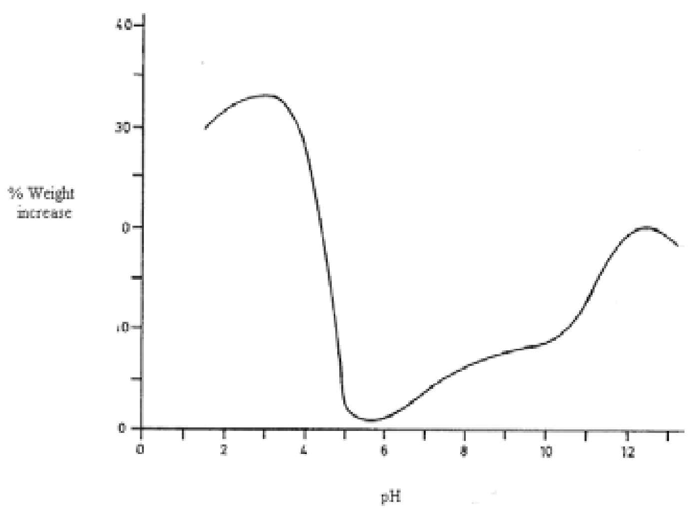
INTRODUCTION

To secure the future of the leather sector it is necessary to drastically reduce pollution and modernize the leather process technology. For a very long time hides and skins have been preserved by salting.[1,2] However, salt must be removed in the later operations and these salts have negative environmental consequences. Drums were introduced in the tanneries circa a century ago and have since been commonly used without any further big improvements in this part of the tanning processes. The tanning industry is a mature sector that produces large amounts of organic residues and effluents as well as necessary chemicals products; with the excess of these materials discharged as waste. The proposal of this work was to reduce such amount of chemicals in number and quantity.

The transportation of wet salted hides is problematic as, for one, the transportation costs includes water, salt and fleshing and secondly, sanitary problems arises including offensive smells. The more critical polluting operations in the leather fabrication are: salting preservation and beamhouse operations. To prevent these problems, an innovative new process is proposed. The treatment starts after the flaying in the slaughterhouse, avoiding the traditional salt curing and the soaking in the tannery. Also, the chemicals for liming are avoided; a biological unhairing process replaces them. Later the pelts are sammied and dehydrated/degreased/dried by solvents in a close loop machine.[3-6] The result obtained is a new dry unhaired pelt, free of chemicals, that is stable, spongy and has no special requirements for storing and commercialization; it can be considered as a new commodity. Also, this allows the tanner to observe the grain surface of the pelts directly for an easier quality sorting.[8-10]

Hide swelling

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



Swelling graphic of pelt at different pH

at pH 5.2. At this pH fibers contain less water. The following chart represents the swelling of the pelt at different pH values.

Collagen groups reactivity

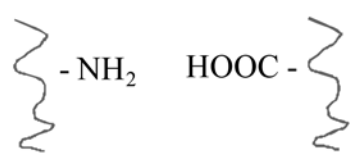
If we dry a delimed and bated pelt, we obtain a hard and translucent material. During the drying operation the collagen fibers are stuck together by electrostatic bonds between the reactive groups of different charges, this forming an internal salt.

Wet fibers in aqueous solution Dry fibers

This material is difficult to penetrate by a solution because the spaces between fibers don't exist. If fibers are maintained separately during a drying process, a spongy, flexible and opaque material is obtained. A technical procedure to avoid fiber bonding is to alter the polarity of the solution. This is plausible by changing the water by an organic solvent. The following table compares the boiling point, the dielectric constant and the heat capacity of water and acetone:

Solvent	Cas Rn	Boiling Point °C	Dielectric Constant	Heat Capacity Cal/G
Water	—	100	80.1	540
Acetone	67-64-1	56	21.1	120

Washing the delimed pelts several times with pure acetone the water contain is reduced, because of the high polarity of the acetone. During the acetone evaporation, the reactive groups are not able to bond between them and the fibers remain separated. As a result, we obtain a fibrous flexible, opaque and white pelt.



Separated dry fibers

Previous Experiences

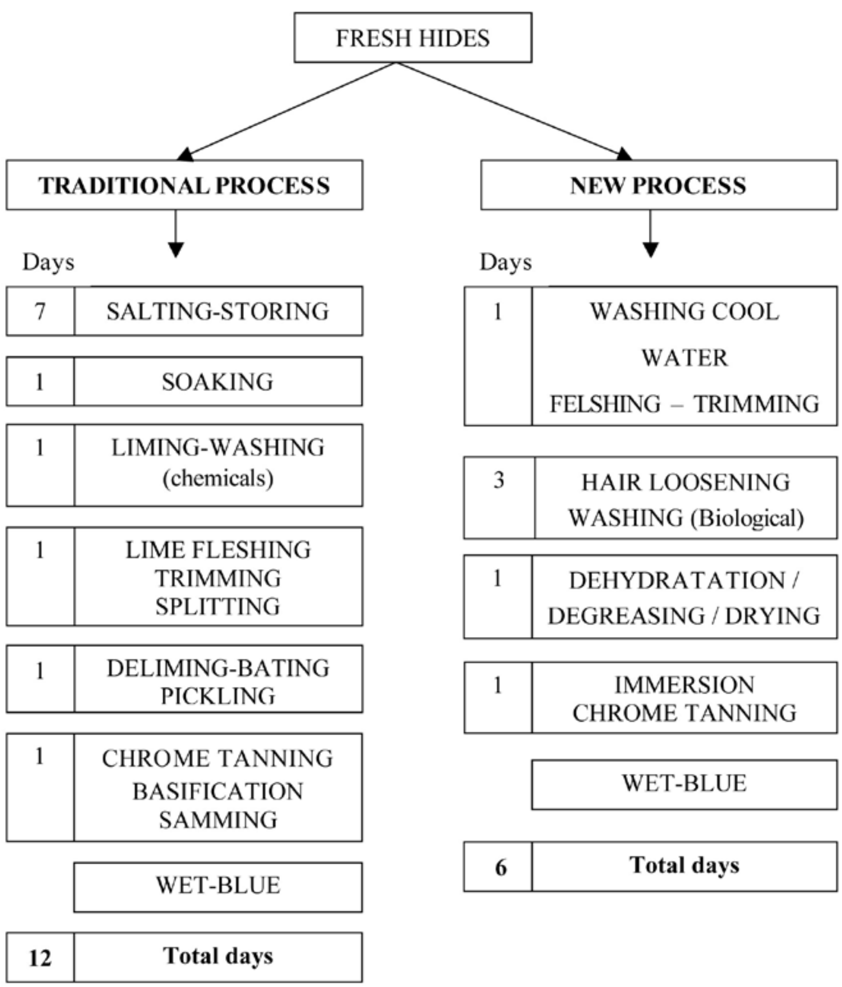
Shearlings, furs and carpet hair-on leathers are not treated with alkaline chemicals to avoid harming the hair, but the final leathers are soft and flexible enough to manufacture e.g. garments. For many types of leather, the unhairing operation is necessary, but can be made by biological systems. Normally leather technicians consider the alkaline liming essential to open the fiber structure, but this is not the unique technique available and known.

In Mazamet, a village of south France, tanneries have used since many years the sweating operation (wool loosing technique) for merinos. Dried or salted skin are soaked and hanged in a chamber with high humidity at 16–22°C temperature, during five days, developing a microbial growth in the flesh side. At the end wool is loosened and removed by a mechanical operation. Skins in live animals contain cells that produce and structure the collagenic fibers. Such cellules are called fibroblast. Once animals are slaughtered the enzymes produced by fibroblasts, in certain conditions and time can damage the fibers of the hides and skins. This phenomenon is known as autolysis.

New process

The basic operations and concepts of acetone dehydration known since 1912 are relatively simple in laboratory conditions. Problems arise, however, when larger scale implementation is attempted. It is necessary to use a modified dry cleaning equipment such as tumbler agitation, centrifugal spin-wringers etc. To make it economically profitable, the dehydration process must be made in a close cycle to recover a high percentage of the solvent. The bated pelts 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 recover the grease. In the following table, we compare a traditional process from raw hides to wet-blue and other directly from fresh hide to wet-blue, through an environment friendly beamhouse process using biotechnology. In the second case, it is obtained BCD as intermediate semi-finished state.



The aim of the new process is to obtain a stable material, which has the following advantages:

- To maintain the sustainability of the tanning industry
- To improve the quality and consistency of the leather
- Reduction the production costs, by saving chemicals, energy and waste treatment
- Reduction of water consumption, therefore, volume of effluents

Fresh hides and skins are processed directly from the slaughterhouse. To avoid spoiling the hides, it is necessary to start the process within the first eight hours after flaying. Hides are washed with cool water in a paddle to eliminate superficial dirt and cooling the hide to facilitate the following fleshing, trimming and, if it is necessary, splitting operations.

The biological treatment to loose the hair is made in a vat using the enzymes contained in the hides and other added microorganisms. The temperature, pH and culture of bacillus are checked and in two days the hides are unhaired. The objective is to activate the enzymes produced by microorganisms, resulting in an ecological process that completely avoids using chemicals. Once the hair and epidermis layer are removed from the grain side, the pelts are washed and ready for a solvent a dehydratation/ degreasing/ drying/ operations in special equipment.

Characterization of BCD

This new material in its dry condition is white, spongy, flexible and opaque, with the appearance of white leather. It only contains collagenic fibers separated at nanometric level without any other chemicals. This is a very light material that can immediately be re-hydrated as it absorbs instantaneously aqueous solution by a simple immersion. The solution penetrates easily throughout the entire thickness of the hide in a few minutes and the mechanical action from drums becomes unnecessary. This new material can be stored for years without special care conditions. Its characteristics are not altered and hygienic safety measures are not necessary. As a non-tanned material, further processes up to finished leather can be adjusted, including production of semi-processed leather as wet-blue, wet-white or vegetable. In Table I, the characteristics of the BCD are compared with a "vachette" (vegetable tanned) and a garment leather (chrome tanned) for an easy comprehension of relative values.

ACETONE TREATMENT SYSTEM + RECTIFICATION OF LIQUID ACETONE + RECOVERING OF ACETONE

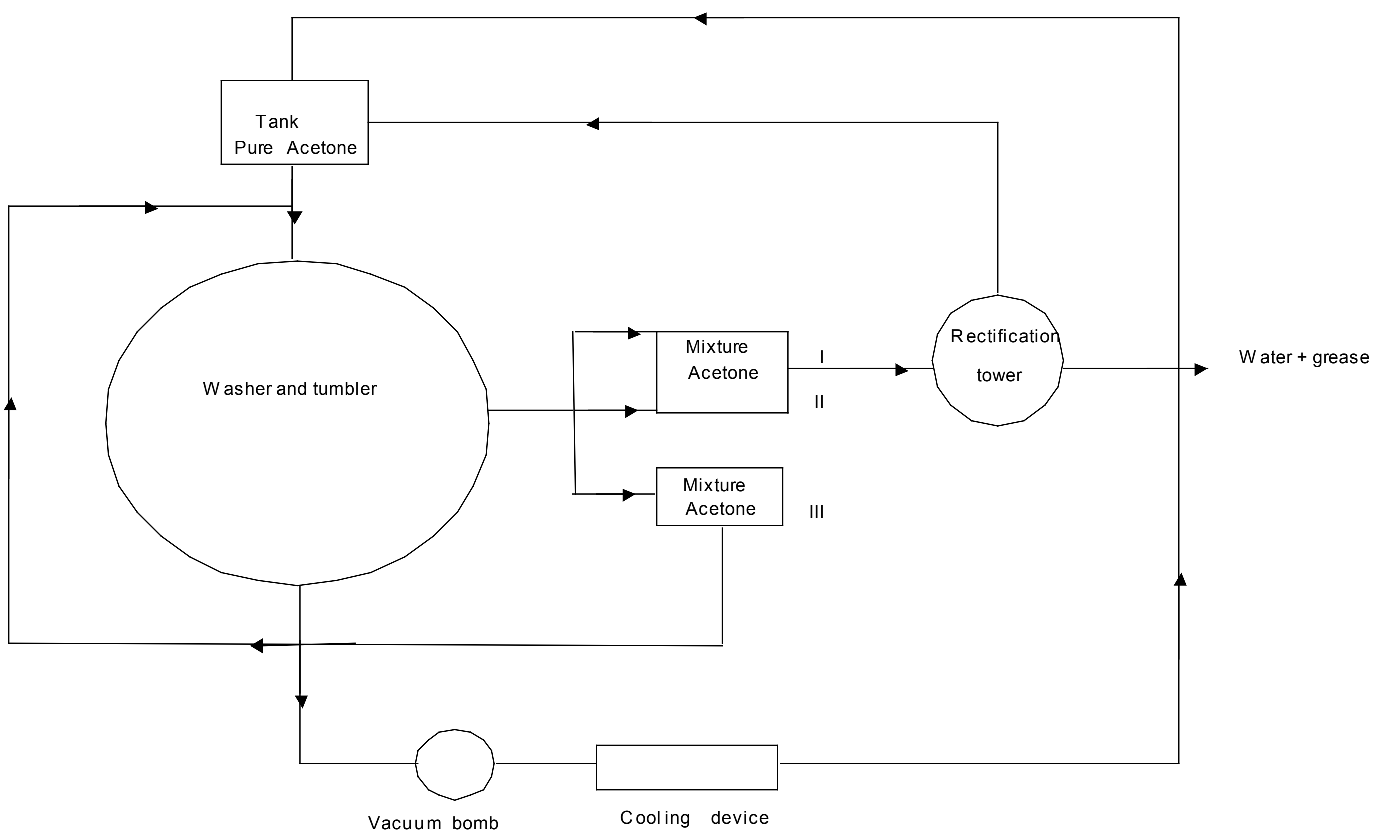


TABLE I

Characteristic of three different 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	°C	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

CONCLUSIONS

- Biotechnology allows avoiding the addition of salt, chemicals and biocides for the preservation of hides and skins directly in slaughterhouses. Therefore, a high amount of pollutants are going away.

- An industrial dehydratation process is proposed after unhairing operations. At the same time, degreasing is also plausible when using fatty skins.

- A dry pelt is obtained (BCD—Biomaterial Collagenic Dehydrated). Such material has several advantages from current leather intermediates:

  1. **Spongy**: solutions can go through the material without mechanical actions.

  2. **Reactive**: the reactive groups of the fibers are immediately very active to bond tanning and retanning materials.

  3. **Free of chemicals**: the BCD contains only collagen.

  4. **Dry**: no water transportation. Facilitates, quality sorting.

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