Improving Tearing Resistance of Leather - Part 1
Prevention and Treatment of Low Tearing Strength in the Tannery

by
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Abstract

An appropriate tear strength is one of the main properties that concern customers and it is also a significant source of claims. The authors make a review of the production process, focusing on each step that can either damage the natural strength of collagen fibers or improve them and therefore, the leather. Although the authors' experience is in bovine hides, the general concepts presented in this paper may be applied to other types of hides and skins.

The aim of this work is to transfer field tannery experiences collected over 40 years of activity in different tanneries, to colleagues that are looking for world class leather production.

Introduction

The physical properties of leather and particularly the tearing strength are recurring problems in tanneries and demand urgent solutions.

Leather is a unique material, having several advantages over other materials and its strength is one of its remarkable attributes.

The massive demand for its supply, force tanneries to process as many hides as possible to conform with customers' orders.

Different strategies had been developed such as chemical products to disguise or cover natural imperfections in order to increase the number of pieces in saleable condition, sometimes lowering its natural beauty through sophisticated finishing procedures.

Furthermore, with the same target, tanneries process heavy weight hides to obtain low substance articles, that could compromise physical properties among them, tear strength.

But there are many other details that need to be taken into account throughout the prolonged and complex leather production process.

Once the problem of low tearing is installed in the tannery, leather technicians must find a quick solution or mitigation, to be able to keep production running while at the same time try to find out the main and subsidiary causes of the problem to make the necessary corrections.

At this point, technicians should want to look for help from experienced colleagues in this field and from leather books and journals. All these activities are time consuming and will delay reaching the answer to solve the problem.

In this work the authors give some basic ideas about which of the critical points to consider once the problem arises, and present some practicalities, theoretical and bibliography derived information from the authors' expertise which should help solve the problem.

This article is divided in 14 Sections:

Part 1

1.0 Collagen as raw material

2.0 Collagen destruction

3.0 Hides preservation

4.0 Soaking

5.0 Dehairing and Liming

Part 2

6.0 Deliming

7.0 Bating

8.0 Pickling,

9.0 Chrome tanning

10.0 How to select stronger hides

11.0 Vessels and mechanical action

12.0 Post tanning operations

13.0 Final Sampling

14.0 Artificial Improvement of Tearing

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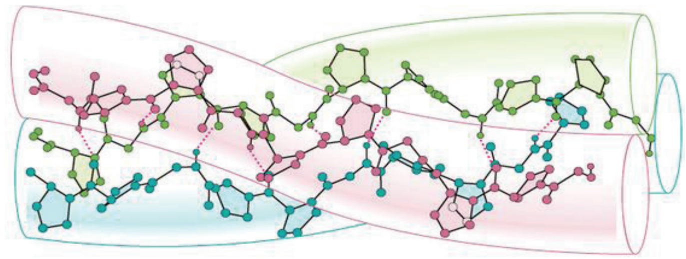

Figure 1. Triple Helix[3]

1.0 Collagen as raw material

1.1 Collagen and fibers[1]

Hides and skins are natural materials of fibrous structure mainly made out of collagen fibers interwoven in a three-dimensional structure, coexisting with other fiber forming molecules like elastin and soluble proteins like polysaccharides and proteoglycans. Collagen is the most abundant body protein, it is present in the skin, tendons, bones, conjunctive tissues, etc. There are several types of collagen. Collagen type I is the major component of hides and skins.

Collagens are characterized by a repeating triplet of amino acids that determine the helical shape of the molecule. The high content of β-amino acids causes the chain to twist into a left-handed helix. Three of these helix twist around each other in a right-handed triple helix that conforms the protocollagen molecule, structure Ramachandran, 1968[2] (Figure 1).

Triple helices bound together in bundles called fibrils that are the smallest units of collagen that are visible under the Scanning Electron Microscope (Figure 2).

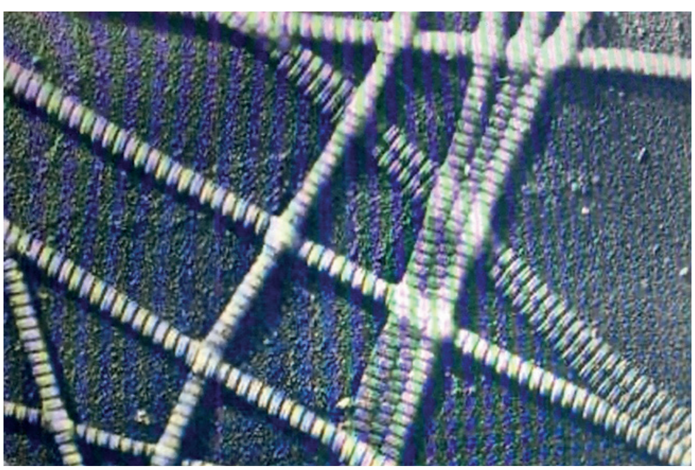

Figure 2. Collagen Fibrils, SEM
Calf Skin Collagen Fibrils 30.000 ×, Dr. J.Gross Collection, Harvard Medical School

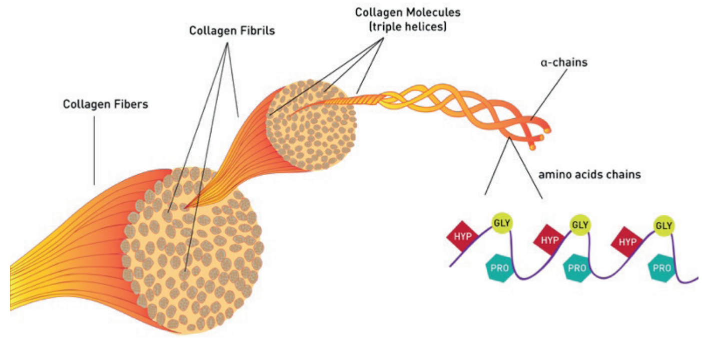

Figure 3. Collagen Structure[4]

Following the hierarchy of collagen structure comes the union of fibrils in the form of fibril bundles and afterwards the bundles come together to create collagen fibers (Figure 3) which are visible to the naked eye.

1.2 Fibers mechanical properties

It is well known that the strength of native collagen, present on fresh hides, is due to its fibrous nature and the ability of fibers and fibrils to slide over one another.[5]

Collagen and hence, hides, skins and leather are anisotropic materials, having different physical properties in different directions. They are strongest in the direction of the component fibers and weakest in the perpendicular direction.

Yang, W. et al., 2015[6] studied the salient micro-mechanisms of deformation and fracture in the skin that appears to have superior tear resistance to other natural materials. They attribute skin's tear resistance to the nano/micro-scale behavior of the collagen fibrils.

Using sophisticated equipment on samples of rabbit skin, the researchers identify and quantify four principal deformation mechanisms acting synergistically, namely:

- Curved fibrils orientate towards the force direction.
- The straightening and the stretching of collagen fibrils.
- The reorientation of fibrils towards the force application direction.
- The sliding of fibrils by the deformation and reformation of bonds between them.

This process is illustrated in the following sequence (Figure 4),[6] under authors permission.

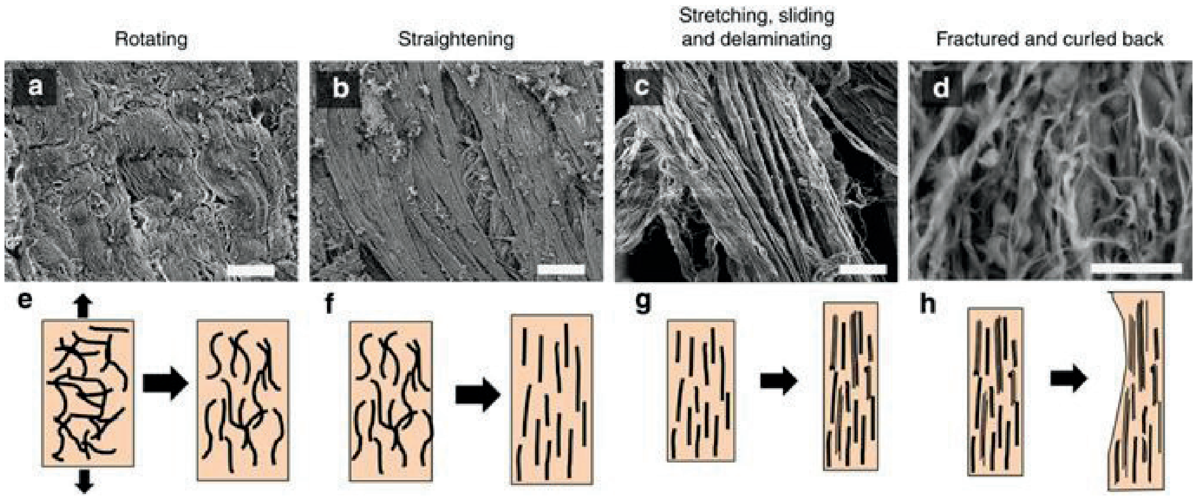

Figure 4. "SEM images **(a–d)** and schematic drawings **(e–h)** of the mechanisms during the four stages of tensile loading of rabbit skin, black arrows in a and e represent the direction of tension testing. **(a,e)** Curved collagen fibrils are oriented along the tensile axis; **(b,f)** collagen fibrils are straightening, larger and larger amount of the fibrils re-orient close to the tensile axis; **(c,g)** collagen fibrils are stretching, sliding, delaminating and orientated completely along the tensile axis; **(d,h)** collagen fibrils are fractured and curled back. Scale bars in a–d are 20, 20, 20, 50 μm, respectively."

1.3 Collagen types

In the diagram by Sharphouse[7] of a cross-section of bovine hide (Figure 5) the CORIUM fibers are composed of collagen Type I, the major component of hides and skins and the GRAIN, by mainly collagen Type III.

Collagen type I has the property to form fibers that interweave creating a strong woven structure resistant to stress in any direction, as mentioned before.

Collagen type III forms finer fibers, less resistant to stress than type I, that compactly bound and form the Grain Enamel, the most valuable part of full grain leather. Under low magnification, this layer appears as a homogeneous film, quite resistant to abrasion, covering the mixture of type I and III fibers underneath, that form the Junction of Grain and Corium. Because of this composition, grain and junction are weaker, less resistant to stress, than corium.

1.4 Species

Kelly et al., 2018[8] studying tear strength and collagen fibril orientation in bovine, ovine and cervine hides and skins, found that cervine leathers had the greatest overall strength followed by bovine and then ovine leathers. Ovine had the greatest variability in strength across the skin.

1. 5 Bovine Hides

In Sharphouse diagram (Figure 5), the weave pattern of fibers in leather shown is quite realistic on average. At the heart of the corium, the fibers are somewhat coarse and vertical, and they become finer and more horizontal as they approach the flesh. The flesh layer is stronger than the corium.

The horizontal fibers (low angle of weave) oppose maximum resistance to tearing force. The vertical ones (high angle of weave), oppose the minimum.

Tournier, 2015[9] in his paper about the evolution of tear resistance during the chrome tanning processes, showed that in normal hides, when split, the grain splits have lower resistance than those of flesh splits. The presence of the horizontal fibers in the flesh splits makes the flesh splits stronger.

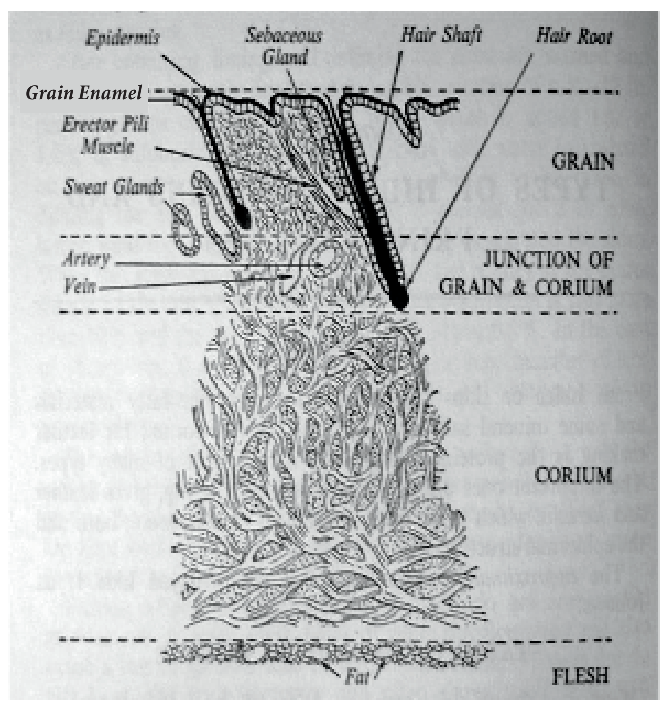

Figure 5. Diagram of cross-section of bovine hide.

Generally normal hides have an average orientation angle of 45° in the corium fibers. This orientation angle varies across each hide and so do the physical properties in different areas. The fibers reach 0° over the flesh side. When fibers in the corium reach 90° hides are known as affected with the so-called vertical fiber defect (VFD).

1.6 Vertical fiber defect, VFD

Amos[10] in 1958, was the first to identify a fiber architecture in hides that produce weak leather, when the fibers of most of the corium are vertical wise. Later, several researchers identified another type of fiber with this condition called high weave fiber defect. Peters and Bavinton, 1982[11] showed that the two forms have a different incidence depending on the breed of the animal. They suggested that whereas vertical fiber is a specific condition (mainly present in Hereford breed because of genetic transmission), high weave is probably one form of the normal weave and concluded that both produce weak leather.

Working with European, North American and South American hides, we found different percentages of weak leather throughout the years and in different tanneries, ranging between 2 to 10%.

Sometimes it is simple to identify areas with VFD by looking at crust leather flesh side, when in the butt region open fibers with cauliflower look, veiny and tearing like paper with edges showing short fibers are seen.

The question is, how to identify or segregate these types of hides early in the tanning process. (See Section 10)

1.7 Cattle breeds, weight, age, sex

Several authors have studied the physical properties of different cattle breeds and their crossings. They found small differences among them. There can be several causes for these differences, namely: age, sex, feeding, genetic, vertical and high weave fiber, climatic conditions, etc.

Regardless of all these, there is a fact that tannery technicians cannot ignore, and this is basically, that it is necessary to process the skins the tannery is able to buy and with the minimum of possible pre-selections.

When it comes to processing salted or brined hides, it is quite normal to classify them in function of weight and sex, but in the case of fresh hides the interval between the slaughter and the starting of the processes must be as short as possible to prevent the hides degradation. Hence, there is not too much time to sort them. In this case, we can apply a general segregation process, for instance bulls and calves or heifers.

In any case, the objective is to start processing those skins as soon as possible, preserving the original natural collagen fibers of the fresh hides without damage.

Betty Haines (1981[12]), studying breed differences in cattle hides, concluded that in undamaged fibers and in a first approximation, physical properties are more a function of original hide thickness than breed or age of slaughter. Thin hides are characterized by a small fiber pattern in the corium and a medium angle of weave (stronger). Thick hides tend to have larger fiber pattern and a higher angle of weave (weaker) as mentioned before in Section 1.6. Therefore, hides from beef cattle are normally thicker than dairy cattle, hence it is expected the latter to be stronger.

We will address this topic further in Section 10.

2.0 Collagen destruction

In this section the main processes that alter the integrity of the collagen fibers and their surroundings are treated and why these alterations result in lowering tearing strength.

2.1 Proteolytic action

This is one of the most dangerous and common sources of tearing problems. It destroys collagen to a higher or lesser degree, in all or part of hides and skins. It is responsible for the appearance of irregularities in the physical properties of supposedly uniform lots of hides.

When e.g., in a lot of fresh or salted hides, hair slippiness is detected, this is a sign that the lot has had excessive time and or temperature exposure after slaughter and this lot has the risk of having low and irregular tearing strength once in crust state. Generally, this comes associated with grain damages, grain looseness and veiny leathers, among other defects.

The delay in starting the soaking, the short time preservation or the medium time salt curing of fresh hides, together with high temperatures, are the root cause of the destruction of collagen fibers by means of autolysis (self-digestion) and bacterial activity.

As soon as the animal dies, the immune system ceases to function and the cells, that all over the body gave life, stop their coordinated work and, out of control, start to destroy the body. The blood vessels with remaining blood are the main sources of enzymes radiation and destruction.

As the hides are flayed, the abattoir handling contaminates the flesh side with bacteria from the hair side. These bacteria find in the flesh side an excellent nutritious media to proliferate and start to travel through the hide thickness, generating additional proteolytic enzymes destroying collagenous fibers, among other things. This process also takes place through grain side injuries or damaged epidermis.

The extensiveness of collagen fiber damage will depend on time, temperature, how dirty the animals were when arriving the abattoir, etc.

2.2 Proteolytic activity
Proteolysis, the breakdown or hydrolysis of proteins into smaller amino acids, takes place under the action of proteolytic enzymes. Among proteolytic enzymes, collagenases are the most important in our matter. They are present in the body and are produced by some bacteria. They break the peptide bonds of collagen that form fibrils, thus weakening the original fibers of the hides and skins and therefore weakening the leathers.

This activity in fresh hides can be measured directly and indirectly by several methods. It can be measured by the increment of soluble Nitrogen (Kjeldahl) of samples of fresh hides, see Figure 7. Or by measuring the hydroxy-proline* content of a water extract of samples of hides before soaking. Also, by microscopic examination.

But the most practical and extended method of controlling the deterioration of fresh hides in tannery is the bacterial count by means of the Standard Plate Count (SPC) technique, with serial dilutions, that reports the counts as colony forming units (CFUs) in 24 to 72 hr. By convenience the results are given as colony forming units per milliliter, CFU/mL. Nowadays, there are rapid tests that give the same result[13] within hours.

Counts of 10^4 and 10^5 are considered normal or with low risk of deterioration, and higher than 10^8 are considered with very high risk. This goes hand in hand with what was mentioned before, that hides with high and very high deterioration not only result in leather with low tearing strength but also with grain looseness, grain damages, veiny leather, etc.

Table I relates levels of risk in relation with the bacterial counts of hides arriving to the tannery. This relation may be used as a guideline to assess the level of risk.

Table I
Bacterial counts vs. Risks of fiber damage.

CFU/mL	Risk
10^4 y 10^5	Low
10^6	Marginal
10^7	High
$> 10^8$	Very high

*Almost uniquely present in collagen.[1]

Lots of fresh hides arriving in these conditions should be labeled in the "tannery traceability system" as RISKY.

It is mandatory that each lot of fresh or short term preserved hides arriving at the tannery must have this type of control or equivalent and keep records for future reference. Similar traceability controls and records hold for long term preservation as we will see later in Section 3.3.

2.3 Traceability
"Traceability in the leather industry, is the capability to keep track of the history of a piece of leather, all the way from the source of the raw hide up to the manufactured leather products, by means of documented, recorded identification", Tournier et al. 2019.[14]

It is the most important requirement for a supplier for making business, and for leather technicians to keep control of production and to investigate what went wrong facing a problem or a claim.

Regarding RISKY lots, it is very important that after evaluation in crust, the results are continuously compared with normal lots in order to confirm the pertinence of the RISKY parameters.

3.0 Hides preservation

This is a crucial step in the leather making process. It is so, because of the vulnerability of the recently flayed hides, the variability of ambient temperatures, the generally long distances between the abattoirs and the tanneries, the complex logistics to bring fresh hides as fast as possible to start the tanning processes and because failures in this step compromise not only physical properties of final leather but also produces other grain disqualifying defects such as loose grain, blemishes, veiny and empty leather, as said before.

Generally, this vulnerable stage for the hides lies outside the control of the tanner.

It is in this critical point where leather technicians must develop a system, that will adapt to each tannery infrastructure in order to protect the labile, valuable and noble natural material that is the collagen network that shapes fresh hides.

The designed system, that will not be cheap at a first glance, must be properly understood and strongly backed by the CEO of the company. It must target the protection of original characteristics of fresh hide collagen fibers, to avoid future problems in different leather properties.

3.1 Fresh hides
In the case of no preservation, hides can stand for the start the tannery process within 4 to 6 hr after slaughter, in hot weather. In the cold, this timing can be extended.

Following graphs in Figure 6 are the results of several years of field experimentation on production lots of fresh hides.

Graph A and B are indicative for batch-lots of hides risking producing leather with low tearing strength, taking into account variations in ambient temperatures and elapsed time in hours, between start flaying in abattoir and start soaking or curing in tannery.

Full line graph A shows the limits between safe and risky lots without any type of treatment, and dotted line B shows the limits for hides cooled at 8-10°C as soon as they are flayed.

For instance, if an abattoir starts the flaying at 6 AM, with 30°C of ambient temperature (horizontal arrows in the graphs), a lot of hides generated during the slaughtering without any preservation, must start soaking in the tannery before 10 hrs. later, vertical arrow, that is 4 PM. If the same hides flayed at the same ambient temperature of 30 °C, are cooled to 8-10 °C as soon as they are flayed, they must start soaking before 26 hrs. later, vertical arrow Graph B, that is 8 AM next day. Lots exceeding these limits must be labeled RISKY of having collagen fibers damages and hence low physical properties, looseness, veininess, etc., because of delay in soaking or curing.

It is advisable that risky lots be directed to low demanded articles, otherwise be examined 100%, once in crust. In the case of tearing strength check piece by piece, by means of a hand dynamometer as it will be discussed later in Section 13.1.

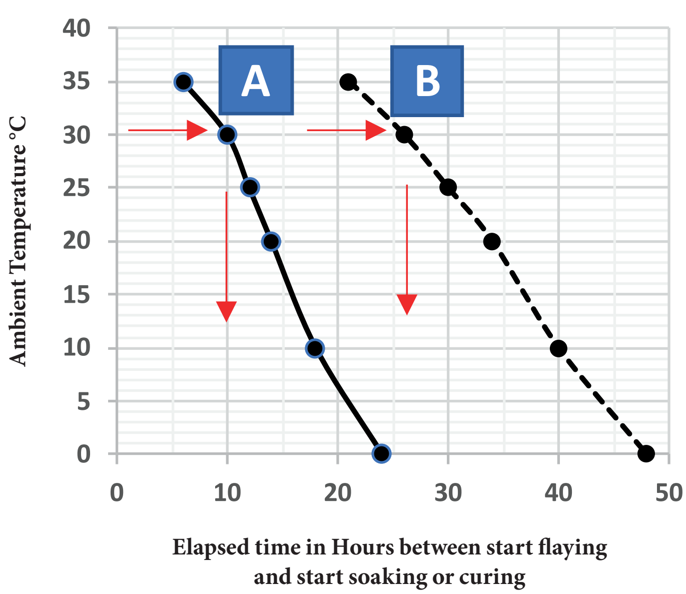

Figure 6. Risk of low tearing leather

3.2 Short term preservation

3.2.1 Cooling

First thing to do after flaying is to lower the body temperature of the hide as fast and as low as possible. If we do this with cold running water, we will wash at the same time bacterial load trapped in the hair and retard the action of autolytic enzymes and remaining bacteria.

As an example, in Appendix I there is the description of a very interesting system that was designed by a tannery and a slaughterhouse, that worked with very good results on leather, during several years.

It was an ecological system, no chemicals added. The thermal inertia of cold hides mass (4-6°C) allowed transport trucks to safely travel several hours, unload at tannery, flesh hair on hides and load soaking drums.

This type of processing slowly increased hides temperature arriving at soaking in between 20 and 25°C.

The temperature control of the lot as well as of individual hides is easily done by hand infrared thermometers.

Up to this moment, we have presented the use of cold as a short-term preservation method, because of the advantages that were mentioned before. But there are other methods to be considered.

3.2.2 Sodium Chlorite

Acidified Sodium Chlorite (ASC) in water produces chlorine dioxide (ClO_2) a strong bactericide, 2.5 times more powerful than hypochlorous acid (HOCl).[15] It is a rather safe microbicide normally used in the food industry; therefore, by-products can be used for food and medicinal purposes. It does not harm hides in normal concentrations or cause problems in effluent treatments. But it does not stop autolysis.

Regarding this product, in 1992 Flores[16] conducted a field investigation with lots of 15 to 30 fresh hides, applying ASC (300 g/l) in different concentrations in immersion tanks, spray gun and tanning drums. Treated hides were left in preservation periods of 24 and 48 hrs. with room temperatures from 24 to 32 °C. One lot without preservation as control.

Based on the information provided in Flores' paper and with the author permission, we have produced the following interesting graphs.

Figure 7 shows the generation of soluble Nitrogen with time in fresh hides without preservation and with different % of ASC. Hides were treated in a tanning drum with 20% water and 0.1%, 0.5% and 1.0% of ASC (300 g/l) with 15 min. of running time.

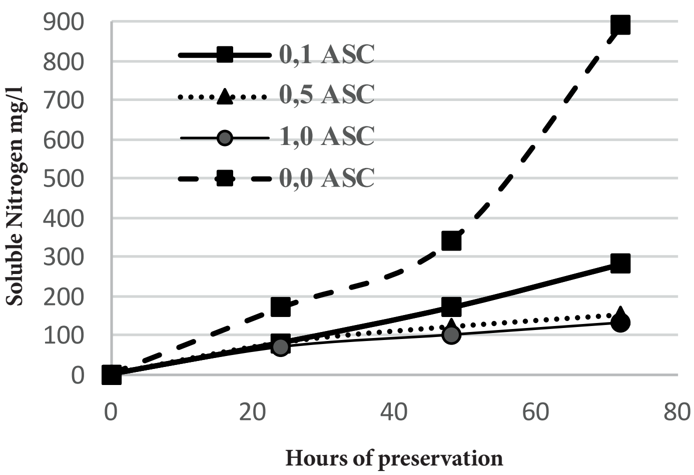

Figure 7. Soluble Nitrogen generation vs. Hours of preservation

After treatment all the hides were processed as usual in the tannery and the final evaluations were done in the crust.

The evaluation of the resistance to tearing was done by IUP 8. Figure 8 shows the evolution of tearing with increasing quantities of bactericide.

Tensile strength has a similar evolution. Therefore, by using an efficient bactericide it is possible to avoid losing important amounts of physical strength.

The paper includes in the crust evaluations, other leather properties as looseness, grain abrasion, etc., that are in line with physical improvements.

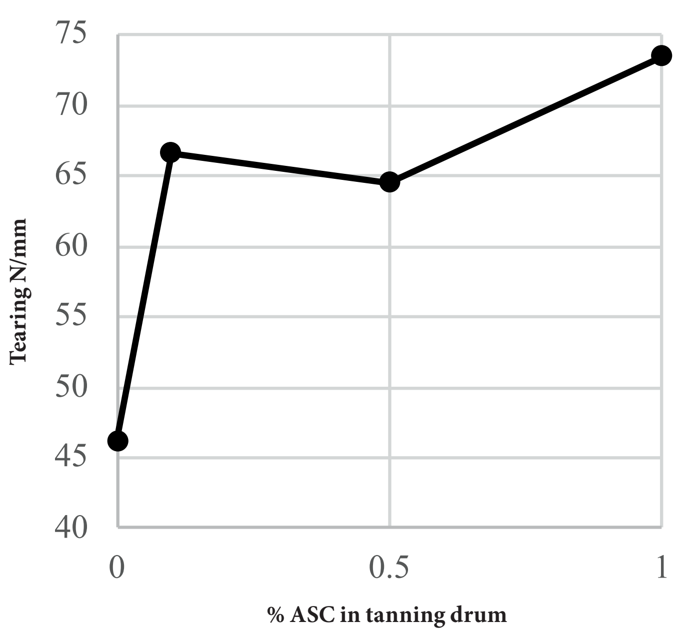

Figure 8. Tearing 24 hr preservation vs. different %ASC

Flores proved that there is a relationship between soluble Nitrogen and proteolytic activity, that reflects in the physical properties and in other grain characteristics.

3.2.3 Other bactericides

There are other commercial bactericides available in the market, some of them include autolytic collagenase enzyme inhibitors. This gives a broader protection to fresh hides.

Each supplier gives precise instructions for their use, but the tannery must be sure that these products are safe for human handling, do not interfere with wastewater treatment plants, and there will not remain residues of them in the by-products that can be destined for animal or human consumption.

3.3 Long term preservation

In this section, only the curing that is attained by the utilization of curing salt or saturated brine solutions is mentioned. These are well known procedures, that will not be treated in detail, but there are some important points to take into account.

- Fresh hides to be salted, must be treated with the same care mentioned before to protect them from autolysis and bacteria, to preserve the integrity of collagen fibers.
- Lots exceeding the limits of Figure 6 regarding elapsed time between start of flaying and salting, must be labelled as RISKY and should be salted apart with proper traceability.
- Even if no delay happened between flaying and salting, there can be irregularities in the salting operation itself, and damages in collagen fibers may occur, so it is mandatory to control salted hides before starting tannage processes.
- Properly cured hides must have moisture content between 40 and 48%, and this moisture must be at least 85% saturated with salt, giving an ash to moisture ratio above 30:100.
- In the authors experience, properly salted hides give slightly higher tearing strength values on average, than fresh hides. This phenomenon can be explained because salted hides, when soaked, never reach the original hydration, so they remain somehow more compact than fresh hides and, if shaved both at same thickness, salted hides have more fibers per millimeter.

Lately in 2019, Sarker et. al,[19] studied at laboratory scale the action of mixtures of different bactericides in sodium chloride solutions with 35% saturation to be applied for short- and long-term preservation. In such paper, there are interesting proposals targeting not only microbial contention but also environmental protection.

In summary, from the authors' point of view regarding protection of the environment and the hides, proper cooling and rapid processing is the best option.

4.0 Soaking

As several authors pointed out, soaking is one of the crucial steps in leather making. And this is true also regarding tearing strength.

In the first place, and according to what was seen before, it is critical to use enough bactericide to keep control of microbial action and to be sure that the enzymes used to speed up the depletion of non-structured proteins do not contain proteolytic enzymes.

Second, Tournier[17] in his paper about soaking control, points out that some of the consequences that a defective soaking can produce are limed or tanned hides showing drawn grain, pronounced growth wrinkles, poor grain, poor handle, scud, poor or uneven softness, difficulties in reaching shrinkage temperature in chrome tanned leather and poor physical properties. Tearing strength is among the poorest physical properties. This is related to problems associated with under soaking due to remnants of Hyaluronic Acid that stick to the fibers when leather is dried and do not let them align along physical stress.

The conclusion is that in this step it is very important to warrant a proper soaking and keep record and control of each lot outcome, labeling as RISKY in the traceability system of the tannery, any lot of leathers that do not comply with the required tannery standard for future reference.

5.0 Dehairing and Liming

At this step, due to working with high pH values bacterial activity ceases to be a problem but again, if enzymes are included in formulations, they must not include proteolytic enzymes.

In such high pH conditions, the hydrolytic reactions are favored and then, hides are subjected to a "controlled damage", as some authors name it. The hydrolysis is directed mainly to eliminate non-structured proteins to produce, together with controlled plumping and swelling, the "opening up of fibers" phenomenon. But some of the collagen is also hydrolysed, mainly the one that was already damaged by autolysis and bacteria in the fresh hide's state. It is possible that the lime hydrolysis tends to complete midway actions started previously by the enzymes.

Liming time is also important regarding the degree of hydrolysis as shown by Gratacos' Graphs,[18] Figure 9. Below 20°C collagen degradation is very low, but generally the process occurs around 26-30 °C or at even higher temperatures. In the liming baths, where there are potassium or sodium hydroxides, the alkaline hydrolysis is more intense. It must be pointed out that in this way the original collagen structure continues to be modified and degraded.

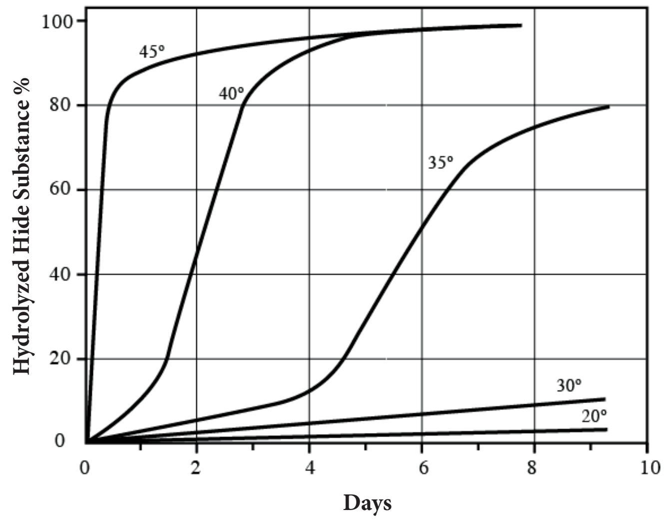

Figure 9. Hydrolysis of hide substance as a function of the time of permanence in saturated calcium hydroxide solution at different temperatures. Bath ratio: 100% on collagen dry weight.

There are three variables that need to be under control at this stage, plumpness, degree of swelling, and time of liming that means prolonged hydrolysis. Plumpness and swelling bind and imbibe water in hides' collagen, these disrupt fiber structure, can exacerbate VFD (Section 1.6) and add to debilitate strength.

Nevertheless, thin leathers for clothing and upholstery can stand longer liming times than tight and thicker shoe upper. For the latter, weekend liming is discouraged, not only for danger of low tearing but also for loose grain.

Despite these previous warnings, Tournier[9] in his paper about evolution of tear resistance in tanning processes, showed that for fresh hides that were cooled down as soon as they were flayed in the way described in Appendix I and processed as soon as they arrive to the tannery, with a well-balanced soaking and liming formulation, the results can be encouraging. Namely, the absolute tearing strength of fresh hides increases when tested after soaking, dehairing and liming. This behavior was explained because the correct opening up of the fibers associated to a proper increase of water content, can lead to a better mobility of collagen fibers, facilitating them to oppose the tearing force.

This speaks about the integrity of original fibers being maintained with proper care of fresh hides and an equilibrated swelling and plumping.

Lots that do not comply with formulations or have long liming times, should be labelled RISKY.

Appendix I

Example of hides cooling at slaughterhouse.

After flaying, hides were water slid to a pressure resistant metal receiver. After 3 to 6 hides, the receiver was closed and immediately subjected to a high-pressure blow of compressed air. The hides travelled approx. 60 m through a 12" diameter metal duct, arriving to a cyclone separator that dropped the hides into the insulated metal cooling pool on the ground. The pool, designed to hold about 1,000 fresh bovine hides, received also ice cubes as hides were dropped.

At the end of slaughtering there was a mixture of hides, ice cubes and water at 4-8°C. A 5-finger crane grabber, helped to mix the contents in order to uniform the temperature and to take hides out of the pool and load the transport truck to the tannery.

The original design of the system used recirculated cold water from cooling equipment because it was the cheapest way to cool down hides. But the buildup of blood and small debris of grease and flesh, clogged separators, filters and cooling coils, making it impossible to go on with it and obliged to change to an ice cube maker machine. The results were fewer problems and maintenance.

Continue in Part 2: JALCA, Volume 117 (1)

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