CHANGES IN TEAR RESISTANCE OF BOVINE HIDES DURING THE CHROME TANNING PROCESS (REVIEWED)

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Abstract.

The tear strength of bovine hides was measured at various stages of the chrome tanning process in order to monitor changes. Tear strength was selected as the physical property that best represents the future performance of leather and reveals the status of collagen fibers after each process step. Tear strength was measured after each of the following steps: fresh hides, limed, lime-split, chrome tanned, wet blue split, and ready to shave. For each hide sample, results were compared to the original strength of the fresh hide. All the tests were conducted in a tannery processing 3000 hides per day, on samples from randomly selected hides within standard production batches. Hide samples were measured in a dynamometer without samples conditioning, at the humidity typical of each processing stage. The results at each stage are discussed, and possible reasons for the observed behavior are proposed.

Keywords: Tear strength, physical properties, fresh hides, liming, limed hides, tanning, lime splitting, wet blue splitting, collagen fibers, interweaving, opening-up, specific resistance, intrinsic resistance, sequential sampling.

1. Introduction

Tear resistance is one of the most critical and controversial physical properties of leather. Deficits in tear resistance are one of the more common customer complaints received by tanneries. Tannery floor technicians are often taken by surprise by clients' observations or claims. They must rapidly analyze the problem to identify the causes and correct the non-conformity, and deliver hides of adequate tear strength to the client as quickly as possible.
Consequently, tear resistance tests are frequently carried out in tanneries, to evaluate the current production batches, the problems arising in leather articles manufacturing and to assess what performance can be expected from hides in practice. These tests are also useful to compare leathers for the same end use.
Identifying critical points in the leather tanning process that affect tear strength is of great interest, but there is little information in the literature. Mention is made of factors that have occasionally increased or decreased tear strength, but reports are often contradictory or not reproducible in practice.
In this paper, tear resistance is studied in specific hides throughout the tanning process in a tannery processing 3,000 chrome tanned bovine hides a day, for use in upholstery and footwear.

1.1 Aims

The goal of this work was to learn more about the effect of different stages of the process on tear resistance, from freshly flayed skins to wet blue ready to shave, and discern where technical interventions could be brought to bear to improve the results.
A preliminary exploratory study was planned, with the following specific aims:

- To study the variations in tear resistance throughout the tanning process, from fresh skins to wet blue ready to shave.
- To compare tear strength patterns in lime-splitted hides against wet-blue splitted full thickness tanned hides.
- To compare tear strength behavior in hides from cows and steers.

2. Materials and Methods

2.1 Hides and tanning processes

Standard tannery procedures were followed. Chilled hides were received in the tannery warehouse where they were prefleshed and then soaked, without enzymes. Liming was done with hair recovery, also without enzymes. These processes were the same for all hides, but tanning procedures were different for lime splitted and wet blue splitted hides. In general, deliming was performed with auxiliaries and ammonium salts, bating was more intense in lime splitted, pickling was done with organic acids and salts (no sulfuric acid used) with 1% oil for lime splitted, and tanning with basic chrome sulfate and magnesium oxide as basification agent. Because of the nature of the assays and the fact they were carried out in a working tannery, no traditional experimental statistical design was performed. Instead, the hides to be followed were chosen at random and a sequential sampling of them was done after each step. Sampling design and procedure are described and illustrated in the following sections.

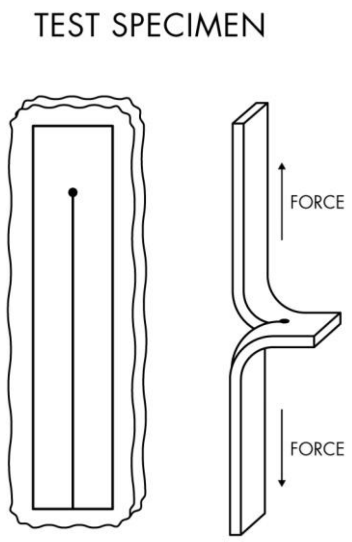

Fig.1 Trouser tear Test

2.2 Measurement of tear resistance

There are two main methods for measuring tear resistance

- Continuous tear or single rip, the trouser or tongue tear (ALCA method E 10)
- Double edged tear (slit or Baumann, SLP 7 or IUP 8).

In this study the trouser tear method (Fig. 1) was used, because it was more suitable for the assays, as described below.

Laboratory tear tests were carried out with an INSTRON dynamometer, model 2519-106. It was decided to take samples and carry out tests using "wet" hides as such, just as they are in the stages of fresh skins, limed and wet blue.

The trouser tear method was chosen because strong clamps could be used to hold the skins, which were slippery and needed to be torn at full thickness, with high forces applied.

The sample surfaces were dried with absorbent paper, to protect the instruments, but when the clamps tightened and began to stretch, some liquid trickled down, so it was necessary to place a fixed absorbent paper under the lower clamp.

Fig. 2 shows the tearing of a fresh skin being tested in the dynamometer.

Fig.2 Skin in dynamometer

2.4 Sampling design

Since the tests to be performed were destructive, the experiments were designed in such a way as to use the minimum number of hides, as required by the tannery. It was decided to monitor the changes in tear resistance in the same hide. That is, sequential measurements were made on each hide at successive stages of the process. It was also decided to take the samples from the official zone, from each half hide.

Samples were taken perpendicular to and 5 cm from the backbone, sized approximately 5 x 18 cm (2 x 7 in) to allow for cutting the trouser test pieces, sized 2.5 x 15 cm (1 x 6 in) (see Fig. 1 and 3). No samples parallel to backbone were taken since several researchers (Carter, 1965; Liu, McClintick and Marmer, 1999) found that tear resistance varies only slightly with the angle of sampling and such variation is not

significant. This author, prior to the study, also confirmed this.
Uncut spaces of between 2 and 3 cm were left between sample holes, so that the sampling zone should not be deformed in later stages (Fig. 5).

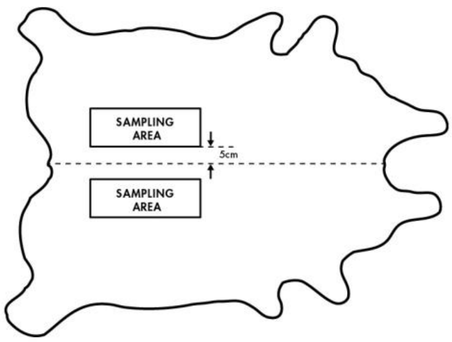

Fig.3 Sampling areas

3. Sampling Procedure on the Shop Floor

Four fresh hides were taken at random, 2 from cows, identified as numbers I and IV, and 2 from steers, identified as numbers VII and X. Sequential samples were taken from the four hides as they were processed (see Fig. 4).

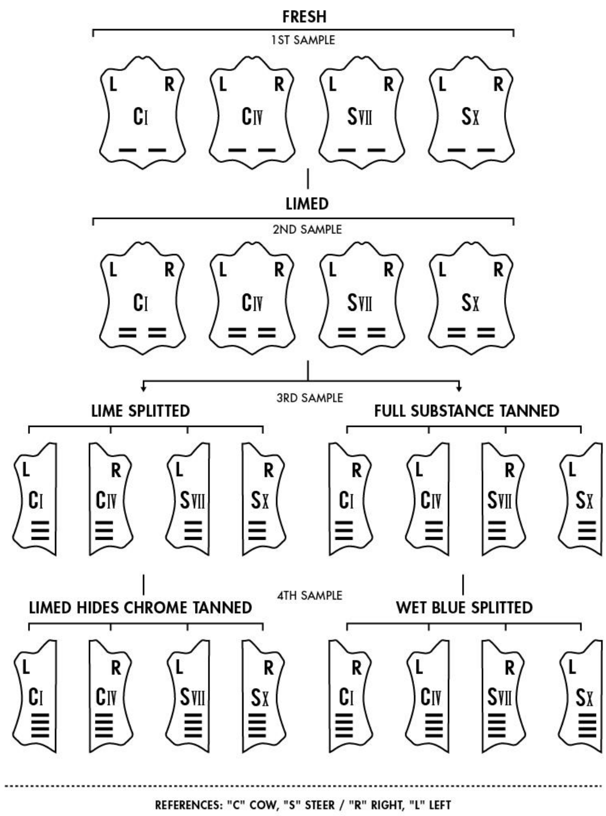

Fig.4 Sampling plan

The following work plan was designed:
Day 1: Samples were taken from fresh pre-fleshed hair-on-hides, cutting out test pieces from the official area on the right (R) and left (L) sides of each hide. The samples were sent to the laboratory for determination of tear resistance and humidity. The hides continued to be processed along with the rest of the production batch of about 400 hides, and were soaked and limed as usual.
Day 2: After removing the hides from the liming bath and after lime fleshing, new samples were cut out from a position adjacent to that of the previous sample. Then the hides were cut into sides.
The left sides of cow IV and steer X, and the right sides of cow I and steer VII, went on to be tanned at full thickness, together with hides in their production batch undergoing treatment with the corresponding full substance chrome tanning formula.
The left sides of cow I and steer VII, and the right sides of cow IV and steer X, were lime splitted and samples were immediately taken from a position adjacent to the previous samples from both the grain splits and flesh splits.

These hides were then tanned together with

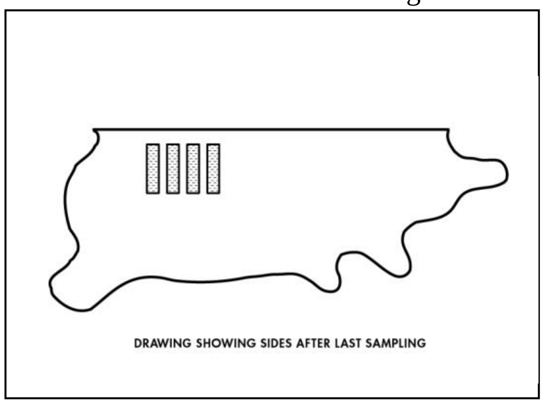

Fig. 5 Final state of sides

the other lime splitted hides in the production batch with the corresponding lime split chrome-tanning formula.
Day 3: After removal from tanning the grain-split sides were wrung, and samples taken adjacent to the previous ones. The sides tanned at full substance were also sampled after wringing, from a position adjacent to the previous samples.
Day 4: Resting day.
Day 5: The full substance wet blue sides were splitted, and samples taken from the grain splits and flesh splits, adjacent to previous samples.

4. Results and Discussion

4.1 Tear resistance of full substance fresh hole hides

Table I shows results for fresh hides. It can be seen that the lowest value of tear resistance in Nn for steer hides is higher than the greatest value in cowhides. Steer hides are significantly thicker than cow hides. SRNT expressed in Nn/mm is significantly higher in steer hides than in cows.

While more data would be needed to draw more valid conclusions, these results strongly suggest:

Full substance cowhides are less resistant to tearing than steers. This can be partly explained by the fact that the hides originate from a meat plant where steers are slaughtered at 2 or 3 years of age, but the cows are breeding animals whose life cycle is over, and are 5 to 7 years old. This age gap between cows and steers is widespread, at least in our region. Heidemann (1993) emphasizes that the mechanical properties of hides depend largely on the age of animals, and in cattle their peak values are at approximately two years. Cowling (1960) and Jenkinson and Nay (1972) also put the age of maturity in cattle at two years.

Table I		Fresh hides results								
		Cow I		Cow IV		Steer VII		Steer X		Total Average
		Left	Right	Left	Right	Left	Right	Left	Right	
FRESH Humidity 65 %	Substance mm	4,9	4,9	4,7	4,8	5,9	5,9	5,5	4,7	5,2
	Force Nn	330	329	290	292	500	345	441	352	360,3
	SRNT Nn/mm	67,3	67,1	61,7	60,8	84,7	58,5	80,7	74,9	69,5
	Average Nn/mm	67,2		61,3		71,6		77,8		69,5
	Average C-S Nn/mm	64,3				74,7				69,5

- **Cowhides are generally of lower thickness than steer hides.** This is a widely recognized and attested fact.
- **The right hand sides of steer hides are less tear resistant than the left hand sides.** As will be seen, this is the case as long as the hides are full substance. Once splitted and separated from the flesh split, the grain layer has reasonable bilateral symmetry, in line with the findings of Beck and Rowlands (1970).
- One of the reasons for this may be that cattle have their rumen on their left side, and when they lie down to chew the cud they do so on their right side, as though to protect their digestive system and therefore the left side of their hide.

4.2 Tear resistance of full substance limed hole hides

Table II is combined with Table I and shows results for both fresh hides and limed hides.

Table II		Limed hides results								
		Cow I		Cow IV		Steer VII		Steer X		Total Average
		Left	Right	Left	Right	Left	Right	Left	Right	
FRESH Humidity 65 %	Substance mm	4,9	4,9	4,7	4,8	5,9	5,9	5,5	4,7	5,2
	Force Nn	330	329	290	292	500	345	441	352	360,3
	SRNT Nn/mm	67,3	67,1	61,7	60,8	84,7	58,5	80,7	74,9	69,5
	Average Nn/mm	67,2		61,3		71,6		77,8		69,5
	Average C-S Nn/mm	64,3				74,7				69,5
LIMED Humidity 70 %	Substance mm	5,8	5,8	5,5	5,5	6,8	7	5,5	5,5	5,93
	Force Nn	350	350	300	278	600	470	400	361	388,6
	Variation Nn	20	21	10	-14	100	125	-44	9	28,4
	SRNT Nn/mm	60,3	60,3	54,5	50,5	88,2	67,1	72,7	65,6	64,9
	Resistance Variation %	5,7	6,0	3,3	-5,0	16,7	26,6	-11,0	2,5	5,6
	Average Nn/mm	60,3		52,5		77,7		69,2		64,9
	Average C-S Nn/mm	56,4				73,4				64,9


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Mean thickness is seen to increase by an average of 0.77 mm, which is 15%.
Cowhides are again less resistant to tearing than steers.
The right sides of steers are again weaker than the left hand sides.

Out of a total of 8 sides, tear resistance increased in 6 and decreased in 2, with an average increase of 28.4 Nn, or approximately 8%. However, as thickness increases, SRNT falls from 69.5 to 64.9, or by 6.6%. This result is consistent with the generally accepted statement that swelling increases the angle of interweaving of the fibers and decreases the specific tear resistance.

4.3 Tear resistance of lime-split hides

Table III	Results up to lime splitting					Averages		
	Sides							
	Cow I L	Cow IV R	St. VII L	St. X R	Totals	Nn	mm	Nn/mm
Fresh hides full subst. Nn	330	292	500	352	1474	368,5	5,1	72,2
Limed grain split mm	2,0	2,2	2,0	2,0			2,1	
Limed grain split Nn	55	82	50	55	242	60,5		29,5
Limed flesh split mm	3,8	3,3	4,8	3,5			3,9	
Limed flesh split Nn	130	137	360	235	862	215,5		55,3
Total Limed Nn	185	219	410	290	1104			
Difference Limed-Fresh Nn	145	73	90	62	-370			
Loss of Resistance after lime splitting vs. Fresh full subst. %					-25,1			

Lime splitting of the four selected sides was carried out with a grain to flesh proportion of 39% to 61%. The grain split is made up of the grain layer and a variable thickness of corium fibers.

The results summarized in Table III indicate a significant loss of resistance after lime splitting.
The mean tear resistance of fresh hides was 368.5 Nn, while the total resistance of lime split grain plus flesh was 276 Nn, indicating that merely splitting the hides caused a loss of tear resistance of 25%.
This Table III also shows that most of the original resistance of the whole hides lies in the flesh side.

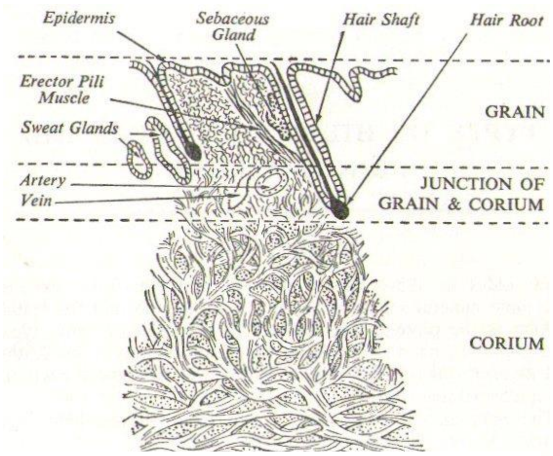

Fig. 6 Diagram of cross-section of bovine skin, Sharphouse (1971)

Loss of tear resistance due to splitting can be attributed to the alteration of the interweaving and branching of collagen fibers that occurs when the hide is split into two layers. It is the branched fibers that are cut, and so their anchor-points are lost and those fibers are left free. If fiber branching occurred in a horizontal direction, i.e. parallel to the surface, there would be hardly any loss of resistance as a result of splitting. The more vertical the branching of the fibers, the greater the loss of resistance.
In the diagram by Sharphouse (1971) of a cross-section of bovine skin (Fig. 6), the weave pattern of fibers in leather is shown quite realistically. At the heart of the corium, it can be seen that the fibers are mostly vertical and that they become horizontal as they approach the flesh side.
The horizontal fibers oppose maximum resistance to force (Covington, 2009). The splitting machine cuts the corium leaving a flesh split with one of its faces being the flesh side of the hide and the other face made up of the cut corium fibers. If the flesh split is re-splitted, the second flesh split is the more tear

resistant because the fibers are mostly horizontal, and the second corium split is the less tear resistant because its fibers are mostly vertical. In practice the second corium split tears so easily that it generally does not resist being processed in a drum. When processing the second flesh split the main shaving must be done on the corium side, exercising extreme care in shaving the flesh side of the split because that is there where the main part of the tear resistance resides.

Table IV SRNT Limed sides	Grain Nn/mm	Flesh Nn/mm
Cow I Left	28	34
Cow IV Right	37	42
Steer VII Left	25	75
Steer X Right	28	67
Averages	29	54

An examination of the SRNT for each of the split layers shown in Table IV indicates that: The grain splits no longer show a difference in tear resistance between cows and steers. This confirms that the differences seen between them in fresh and limed hides were due to the relative resistance of the flesh splits.

The fact that the SRNT of cow grain split is found to be equal to or greater than that of steers may indicate that the grain layer of cows is thinner than that of steers, and therefore at an equal thickness, cow grain splits retain more corium than those of steers.

4.4 Tear resistance of lime split hides after chrome tanning

After lime splitting the sides were tanned according to tannery procedure. Tear resistance results in samples after tanning and wringing are shown in Table V.

The mean values obtained show a 13% drop in tear resistance. This result was not statistically significant and needs to be confirmed with further experiments and more samples.

4.5 Tear resistance of full thickness hides after tanning and chrome splitting

Table VI shows that the simple act of tanning a full thickness hide decreases tear resistance by 40%.

Table VI	Results up to chrome tannage							
	Full substance Sides					Averages		
	Cow I R	Cow IV L	St. VII R	St. X L	Total	Nn	mm	Nn/mm
Fresh Hides full subst. Nn Humidity 65%	329	290	345	441	1405	351	5,3	66,9
Limed Hides full subst. Nn Humidity 70%	350	300	470	400	1520	380	6,0	63,9
Wet Blue full subst. Nn Humidity 52%	203	125	279	238	844	211	5,0	42,4
Loss of Resistance from Fresh to Chrome Tannage %					-40			

It can be deduced that tanning the grain layer of a lime split pelt should also decrease tear resistance, but to a lesser extent than for the full thickness hide. This would be consistent with the 13% loss of resistance seen in Table V above, which may therefore be correct.

Wet-blue splitting of the 4 corresponding sides was carried out with a grain-flesh proportion of 40% to 60% (very close to the 39% to 61% of the lime split). Results are shown in Table VII.

Table V	Results up to chrome tannage							
	Splitted Limed Sides					Averages		
	Cow I L	Cow IV R	St. VII L	St. X R	Totals	Nn	mm	Nn/mm
Limed Grain Split Nn Humidity 70%	55	82	50	55	242	61	2,1	29,5
Tanned Grain Split Nn Humidity 50%	50	50	45	66	210	52	2,1	25,5
Loss of Resistance after chrome tannage %					-13,26			

Table VII	Results up to Wet Blue Splitting							
	Sides					Averages		
	Cow I R	Cow IV L	St. VII R	St. X L	Total	N	mm	N/mm
Wet Blue full subst. Nn Humidity 52%	203	125	278,9	237,9	844	211	5,0	42,4
WET BLUE SPLITTING								
Tanned Grain Split mm	2,00	1,70	2,30	2,00			2,0	
Tanned Grain Split Nn Humidity 50%	50	35	48	52	185	46		23,1
Tanned Flesh Split mm	2,25	2,05	3,80	2,50			3,0	
Tanned Flesh Split Nn Humidity 50%	99	62	173	106	440	110		37,0
Total Nn	149	98	225	161	625			
Difference Nn	-53	-26	-54	-77	-219	55		
Loss of Resistance after wb splitting %					**-25,9**			

This process also significantly decreased tear resistance.
Simply splitting the wet blue led to a loss of 26% of tear resistance. This is similar to the loss of resistance of 25% after lime splitting.
The closeness of these values is probably due to the same phenomenon: alteration of the collagen interweaving when a hide is split into two layers.
According to experimental data, when the grain split layers have been tanned, those that were lime splitted are more resistant than the wet-blue splitted, by 25.5 to 23.1 Nn/mm, respectively, amounting to a difference of 9% (see Tables V and VII).

Possible reasons for this are, on the one hand, the 1% fatliquor added during tanning, and on the other, that lime split hides can stretch in some degree in the tanning drum, freeing the fibers, which are rearranged into a more horizontal weave pattern. Part of the loss of resistance due to the tanning process is compensated for by the rearrangement of the fibers. This may also explain the typical nature of finished leathers originated from the **lime splitting tanning**, which have a more open fiber structure, are softer, have lost less physical resistance, have a larger surface yield and a tendency to grain loosening, providing leathers more suitable for upholstery.
However in **full thickness tanning**, the presence of the flesh side of the hide prevents stretching, so the fibers cannot be rearranged. They are tanned in place, and this gives rise to other features of full thickness tanned hides such as the tendency to draw, to accentuate neck and fat wrinkles, and to have a more compact corium structure, firmer grain and lower surface yield, providing leathers more suitable for footwear manufacturing.

5. Recapitulation

In sum, in this tannery chrome tanning processes tend to reduce tear resistance in leather. In full thickness tanning, the decrease in tear resistance is greater.
Nevertheless, as we said before, if we look at the tearing resistance of fresh and limed full substance hides, there is an increase of resistance in limed hides but a decrease when is calculated the resistance per mm, as explained in section 4.2
The explanation of the increase in resistance after liming full substance hides can be because the opening up of the fibers associated to the increase in water content. Both phenomena can lead to a more and better mobility of collagen fibers, facilitating them to oppose the tearing force.
In hides tanned after lime splitting, reduction of tear resistance is lower, probably because the decrease in resistance due to tanning is compensated for by rearrangement of the fibers.
Below, we study changes in the tear resistance of the 2 mm grain layer, which is used for producing most leather articles.
We will graph the evolution of SRNT for the 2 mm along the steps of each process, lime and blue splitted.
In the two types of splitting, the splitted layers had around 2 mm thickness; but in the steps where the 2 mm were forming part of the full substance of the hides, it was not

possible to measure the tearing resistance, anyway we have some data from which it is possible estimate it.
We define the Intrinsic Resistance (IR) as the resistance of a layer of a hide or leather while is resting in a un-splitted state.
A new couple of terms are introduced; we call the estimated values Intrinsic Resistance (IR) expressed in Nn and Specific Intrinsic Resistance to Natural Tearing (SIRNT) in Nn/mm.
To estimate the IR we take the measured value of the tearing resistance after splitting and increase it with half of the splitting loss.
We estimate that the splitting loss is distributed equally between grain and split layers.
In Fig. 7 is given a schematic representation for TR, IR and SIRNT.

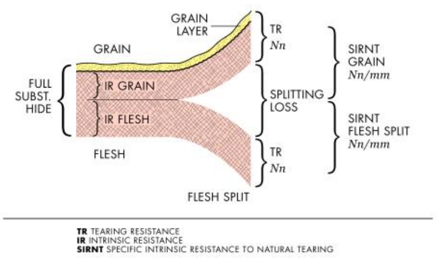

Fig. 7 Schematic representation of TR, IR and SIRNT

5.1 Estimation of IR and SIRNT of grain layer of limed hides.

In the case of lime splitting, the average value of the Tearing Resistance of the grain layer is 60,5 Nn and the splitting loss is 92,5 Nn (See Table III)
The IR for the 2,05 mm layer is 60,5 + 92,5/2 = 106,8 Nn
The SIRNT is 106,8/2,05 = 52,1 Nn/mm
This value holds for hides involved in both processes, lime and wb splitted.

5.2 Estimation of SIRNT of grain layer of fresh hides

The previous calculation allow us to estimate that the average value 106,8 of IR of limed hides is equivalent to 27,5 % of the value of full substance limed hides (388,6 Nn, see Table II).
We can assume that the same % applies to estimate the IR of fresh hides based in the Tearing Resistance of full substance fresh hides (360,3 Nn, see Table II)
Thus the IR for a 2 mm layer of fresh hides would be 360,3 x 0,275 = 99,0 Nn
And the SIRNT 99/2 = 49,5 Nn/m
This value also holds for both processes.

5.3 Estimation of SIRNT of grain layer of full substance tanned hides.

In the case of wet blue splitting, the average Tearing Resistance of the grain layer is 46 Nn and the splitting loss is 55 Nn (See Table VII)
The IR for the 2 mm layer is 46 + 55/2 = 73,5 Nn
The SIRNT is 73,5/2 = 36,7 Nn/mm
The measured and estimated values of above are represented on the following graph, Fig. 8.

5.4 Measured SRNT values in the graph

The values for the lime splitted process and subsequent tannage are in Table V, 29,5 and 25,5 Nn/mm respectively.
For the wb splitted is in Table VII: 23,1 Nn/mm.

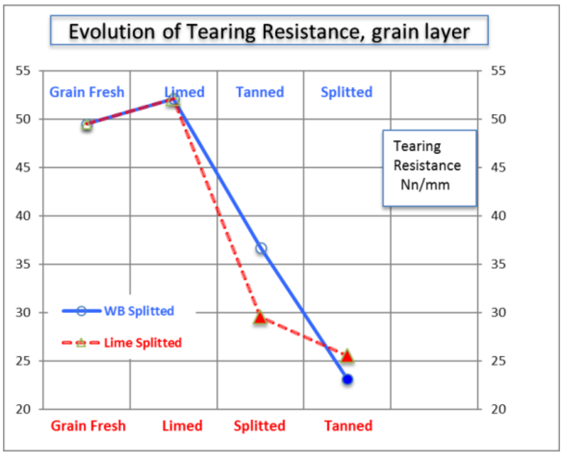

Fig. 8. SRNT and SIRNT in both experiments at different processing stages.
Filled symbols: Measured SRNT values. Open symbols: Estimated SIRNT values.

6. Conclusions and recommendations

In accordance with the aims and conditions of the present paper, the study findings demonstrate that leather processing in this tannery leads to reductions in tear resistance.

Both machine operations, lime splitting and wet blue splitting lower the resistance in about 25% each one. Since this is due to mechanical disruption of the interwoven collagen fibers, it is unlikely that this loss of tear resistance can be diminished. This is consistent with Wilson

and Merrill (1931) who mentioned that the sum of the resistance of the parts of a split hide is never as great as that of the whole hide, confirming the negative effect of cutting through the collagen structure, but not giving magnitudes of the changes.

Tanning full thickness limed hides reduced tear resistance by 40%, whereas tanning lime split hides reduced it by approximately 13% (to be confirmed). Among the chemical processes involved in tanning (deliming, bating, pickling and tanning), there are, no doubt, opportunities for improvement. Processing of lime split hides produces leathers with somewhat higher tear resistance than wet-blue split hides.

The differences in tear resistance between cow and steer hides, evident in fresh skins and full thickness limed pelts, practically disappear in the grain layer after splitting. The differences in tear resistance between left and right sides of fresh and full thickness limed steer hides also disappear after splitting. In general, the original differences in thickness of whole hides remain in the flesh side, and most of the tear resistance resides in the corium of the flesh side.

It is crucially important to protect the state of the collagen fibers at all times. Good conservation practices should be used so that freshly flayed skins reach the soaking stage undamaged. Tannery technicians must be constantly aware of situations that might alter the state of the collagen, and therefore reduce the resistance of the fibers. Any process that incorporates more corium fibers into an equal thickness of the final leather will improve its resistance.

Among the tanning processes implemented by this tannery there are opportunities to improve the physical properties of leathers, that is, **to cause less damage and preserve more of the properties of the original hide collagen fibers.**

The methodology used in this study has proven to be simple and useful for any tannery to:

- Investigate the effects of its processes on the collagen fibers
- Compare different processes in house or between tanneries,
- Compare changes in processes and chemical products,
- Compare different raw hides, categories and types,
- Compare different fresh hides preservation methods

It is relatively easy, and although it involves destructive sampling which has a cost, this can be regarded as minimal compared to the technical advantages that can be obtained.

With this method it is possible to do research work at tannery level.

Acknowledgements

I thank Marcel Branáa of Curtiembre BRANAA for allowing these experiments to be carried out; Nicolás Martínez and Salvador Kuz, also of Curtiembre BRANAA, for their active participation in the work in the tannery; Dr. Mónica Cadenazzi of the Statistics Department, Facultad de Agronomía, UDELAR, Uruguay for her help with statistical treatment of the data; and Victor Daniel Vera, formerly of CITEC, Argentina, Germán Azzato, Jaime Velez and Juan Carlos Oclepo of SADESA Group International and Juan Carlos Pérez of Daxilan, Uruguay, for corrections, suggestions and constructive criticism of the text.

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