Salt-free Chromium Tanning: Practical Approaches

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Abstract

Chromium tanning finds a prominant place in leather manufacturing for permanent stabilization of hide/skin matrix. Though, it has multiple advantages in terms of high thermal stability, easy process and low cost etc., the current practice is not environmentally sustainable. Poor chromium exhaustion and TDS load generation are the major environmental threats of conventional chromium tanning system. On the other hand, salt-free chromium tanning is identified as one of the efficient alternative approaches for hide/skin matrix stabilization. However, it has not been commercially practiced due to the several practical difficulties. In this work attempts have been made to develop a practically viable high-performance salt-free chromium tanning system using deliming liquor as tanning float and changing the order of addition of masking salt. The developed methodologies completely avoid the use of salt/basification process and it is suitable for all kinds of raw materials and tannery houses. Besides, the process enjoys 71-77% reduction in TDS load and the uptake of chromium is around 90%. The physical strength characteristics are on par with conventional process and the leathers exhibit good grain tightness and roundness. The developed methodologies are simple and do not require any specialty chemicals.

Introduction

Tanning is an important unit process of leather manufacturing, which imparts permanent stability to the hide/skin matrix against microbial degradation and improves the thermal stability/ functional properties. Tanning systems based on chromium(III), aluminium(III), zirconium(IV), plant polyphenols, aldehydic compounds, triazine and epoxides have been developed in which chrome tanning is versatile.[1] Today, 85-90% of global leather production is based on chrome tanning.[2] The fundamental reasons for practicing chrome tanning to a larger extent are (i) high shrinkage temperature (ii) formation of stable crosslinks (iii) multipoint fixation leads to high range ordering (iv) high stability against alkali precipitation (v) easy process (vi) low level risk in process control and (vii) economically cheaper than other tanning systems.[1] Though chrome tanning is classified as a versatile tanning system, the current practice is not environmentally sustainable. The uptake of chromium(III) in conventional method is about 55-65% w/w and the remaining is discharged into wastewater stream at a concentration of around 3000 mg/liter.[3] Therefore, the implementation of chromium recovery systems is mandatory to meet the discharge norms of about 2 mg/liter. In addition, sodium chloride used in the pickling process increases the TDS load in final wastewater. The removal of TDS from wastewater requires sophisticated end-of-pipe treatment systems like reverse osmosis (RO) which in turn increases the treatment cost. In addition, sodium chloride recovered from treatment process is contaminated with other mineral salts. Therefore, a special treatment system needs to be adopted to recover the sodium chloride which in turn further increases the treatment cost. The statistics show that the global tanning industry generates approximately 27.5 billion liters of spent chrome tanning liquor containing 24 kilotons of chromium(III), 340 kilotons of chloride (Cl^-) and 270 kilotons of sulfate (SO_4^{2-}) per annum. Out of which, the pickling and tanning process alone contribute 71% of chromium(III), 43% of chloride, 50% of sulfate and 20% of water.[4] In the last decade, several attempts have been made to resolve the problems associated with conventional chromium(III) tanning systems. Some of the developed technologies and the salient features are given in Table I.

In addition, several chrome-free tanning agents like diazine-based compound, modified glutaraldehyde and polyaluminium silicate etc. have been developed. However, none of the tanning systems are equivalent to that of chrome tanning process. Based on the literature survey in the area of improved chrome tanning process, it has been identified that the "Salt-free chromium tanning" would be an ideal approach, which meets both tanning performance and environmental sustainability. Though scanty attempts have been made on salt-free chromium tanning system, the technology was not commercially/ practically successful and the possible reasons would be

1. Non-suitability for thicker hide
2. Closer monitoring of process
3. Requirement of skilled labor
4. High risk for quality control

In order to obviate the above problems, in this work an attempt has been made to utilize the neutral salt formed during deliming process for pH reduction and the ionic strength of the solution was increased by reducing the float volume. Another approach was developed where masking salt was used before acidification, so that it may act

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Table I.
State-of-the-art technologies for improved chrome tanning system

S.No	Technologies	Salient features
1	Usage of exhaust aids	Dicarboxylic or polycarboxylic acid[5] or protein hydrolysate[6] was used in tanning to improve the chromium(III) uptake. The maximum uptake efficiency was around 85%. Problem associated with pickling process has not been resolved
2	Ethanolamine pre-treatment	In this technique, pickled pelt was treated with mono ethanolamine followed by BCS. The maximum uptake efficiency was around 85%.[1] Problem associated with pickling process has not been resolved
3	Aluminum pre-treatment	After pickling process, the pelt was treated with 2% aluminum sulfate followed by BCS. The presence of aluminium(III) salt in tanning process improves the degree of chromium fixation in such a way that decreasing the activation energy and the maximum efficiency was around 85%.[7] Problem associated with pickling process has not been resolved
4	Increasing the carboxyl group of hide/skin matrix	In this method, formaldehyde and malonic acid reacted with hide/skin matrix via Mannich and Michael reaction to generate carboxyl moiety at the end terminal of basic amino acid. The maximum efficiency was around 80%.[8] Problem associated with pickling process has not been resolved
5	Non-aqueous tanning	In this technique, pickled pelt was treated with BCS in the presence of organic solvent[9-14] or wax or supercritical fluid.[15] The uptake efficiency was near 100%. Problem associated with pickling process has not been resolved
6	Chrome tanning at high pH (Pickle-free approach)	pH of the delimed pelt was adjusted to around 5.5 using organic acid followed by BCS treatment. The uptake efficiency was about 85-90%[16]

as buffering agent during acidification as well as masking salt in chromium tanning process.

Materials and Method

Wet-salted cow hides were conventionally soaked and further subjected to drum liming process (Water – 300% w/w, Lime – 5% w/w and Sodium sulfide – 3% w/w). The fleshed limed pelts were used as raw materials for salt-free tanning process. All the chemicals used for leather processing were of commercial grade. Analytical grade chemicals were used for analysis purpose.

Practical Approaches for Salt-free Chromium Tanning

Two different salt-free tanning approaches have been attempted and the detailed process recipes are given in Table II & III. In each approach, 5 cow limed pelts were cut along the backbone. The left halves were subjected to salt-free tanning process and right halves were subjected to conventional pickle-based chrome tanning process. The process recipe for conventional chromium tanning process is given in Table IV. All the trials were validated at CLRI-Pilot tannery with the scale 100 kg/batch.

Analysis of Wet-blue Leathers

Thermal stability of the wet-blue leathers obtained from each tanning system was analyzed using shrinkage temperature measurement. SATRA STD 114 shrinkage tester was used to measure the hydrothermal stability of wet-blue leathers. Surface morphology of the wet-blue leathers were analyzed through Celestron Handheld Digital Microscope.

Analysis of Physical Strength Characteristics and Organoleptic Properties

The specimens for various strength characteristics such as tensile strength, % elongation at break, tear strength, grain crack load, and distension at grain crack were obtained as per IULTCS standard methods. All the specimens were conditioned at 25±1 °C and 65% RH for 24 hrs. before the analysis. The organoleptic properties of final leathers were analyzed by experienced personal and rated on a scale of 1-10, where higher the value better the properties.

Analysis of Wastewater

The composite liquor (deliming to tanning) collected from each tanning system analyzed for chromium content and TDS as per the standard the procedure.

Table II

Process recipe for salt-free chromium tanning in deliming liquor (CTDL)

Process/Chemicals	% Offer	Time	Remarks
Raw material: Cow limed pelts, Thickness (Neck): 8-10 mm			
Washing			
Water	100		
Hydrogen peroxide	0.3	30 min	Washed thoroughly and drained
Deliming			
Water	0		
Ammonium chloride	3	120 min	Zinc acetate test for the presence of sodium
Hydrogen peroxide	0.3	30 min	sulfide. Completion of deliming checked by
Bate	0.5	30 min	phenolphthalein indicator
Acidification			
Sulfuric acid	0.8	4 × 15 + 120 min	pH adjusted to around 5.0 - 5.5 and aged for
Water	10		120 min under static condition
Chrome tanning			
BCS	6	5 hr	Initial pH: 5.0-5.5
Sodium formate	1		Final pH: 4.0
Fungicide	0.1		Cross section was checked for penetration
			Drained and piled.

Table III

Process recipe for salt-free chromium tanning: changing the order of addition of masking salts (COAMS)

Process/Chemicals	% Offer	Time	Remarks
Raw material: Cow limed pelts, Thickness (Neck): 8-10 mm			
Washing			
Water	100	15 min	Washed thoroughly and drained
Deliming			
Water	100		Completion of deliming checked through
Ammonium chloride	3	120 min	phenolphthalein indicator. Drain
Alkali bate	0.5	30 min	
Washing			
Water	100	45 min	Washed thoroughly and drained
Masking salt Treatment			
Water	40		
Sodium acetate	1.5	15 min	
Acidification			
Formic acid	0.5	30 min	pH adjusted to around 5.0 and aged for
Water	5		180 min under statistic condition
Sulfuric acid	0.5	3 × 10 + 30 min	
Water	10		
Chrome tanning			
BCS	6		Initial pH: 5.0-5.5
Sodium formate	0.5	3 × 15 + 120 min	Final pH: 4.0
Fungicide	0.1	5 hr	Cross section was checked for penetration.
			Drained and piled

Table IV

Process recipe for conventional pickle-based chrome tanning

Process/Chemicals	% Offer	Time	Remarks
Raw material: Cow limed pelts, Thickness (Neck): 8-10 mm			
Washing			
Water	100	15 min	Washed thoroughly and drained
Deliming			
Water	100		
Ammonium chloride	3	120 min	Completion of deliming checked through
Alkali bate	0.5	30 min	phenolphthalein indicator
Washing			
Water	100	30 min	Washed thoroughly and drained
Pickling			
Formic acid	0.5		
Water	10	30 min	
Sulfuric acid	1.0		
Water	10	3 × 15 + 150 min	pH: 2.8-3.0
Chrome tanning			
BCS	8	2 × 30 + 180 min	Check Penetration
Basification			
Sodium formate	1	2 × 5 min+ 30 min	
Sodium bicarbonate	1.25		
Water	10	4 × 10 min + 180 min	pH: 3.8 to 4.0, Drain & pile
Fungicide	0.1	30 min	

Results and Discussion

Approach-1: Salt-free Chrome Tanning in Deliming Liquor (CTDL)

In salt-free chrome tanning system, pH of the pelt is reduced from 8.5 to 5.5 prior to chromium treatment. Whereas in conventional pickle based tanning system the pH is around 3.0 prior to chromium treatment. Since the acidity of salt-free tanning system is low when compared to conventional tanning, the salt concentration or ionic strength required to prevent the acid swelling in tanning system need not be high as like pickling process.

Conventionally, ammonium salts are predominantly used for deliming process and the spent liquor contains unreacted ammonium salt as well as some amount of calcium salt, which is formed during the neutralization process. It is estimated that the salt concentration (TDS) of spent deliming liquor is ranging from 2.5-3.0% (Deliming float: 100%). Hence, in this work a process has been designed to utilize the salt present in deliming liquor for acidification without employing additional salt to the tanning system. More specifically, the delimed pelts have been subjected to acidification process in the same float without washing and subsequently treated with chromium. In this method, the float volume of deliming process is reduced to 50% to increase salt concentration in the system. One of the risk factors in the developed process is that conversion of sodium sulfide carry-forwarded from liming process into toxic hydrogen sulfide gas. The formation of H_2S can be avoided by oxidizing the sulfide into sulfate by using hydrogen peroxide. In this method, hydrogen peroxide has been used in two different stages such as washing (before deliming) and at the end of deliming process for effective sulfide oxidation. The absence of any residual sulfide in the system was ascertained through zinc acetate test prior to acidification process. On the other hand, deliming liquor also contains some amount of dissolved ammonia that may be converted into ammonium salt during the acidification process. It is also found that the concentration of salt in spent deliming liquor is 3.5% w/v and the conductivity of the liquor is around 40 ms/cm (B_e^o: around 2.5). Therefore, the salt concentration is sufficient to avoid the acid swelling during acidification. The pH adjusted pelts were treated with BCS without any further treatment. In this method, 6% BCS was given in one feed, which resulted in faster diffusion of chromium into the matrix. Shrinkage temperature of the wet-blue leather was found to be 104°C which is on par to the conventional wet-blue. It is also found that the chromium exhaustion was around 90% w/w.

Approach-2: Changing the Order of Addition of Masking Salts (COAMS)

Another approach for pickle-free chrome tanning has been developed by changing the order addition of masking salts. Conventionally masking salts are added during the basification process and its role

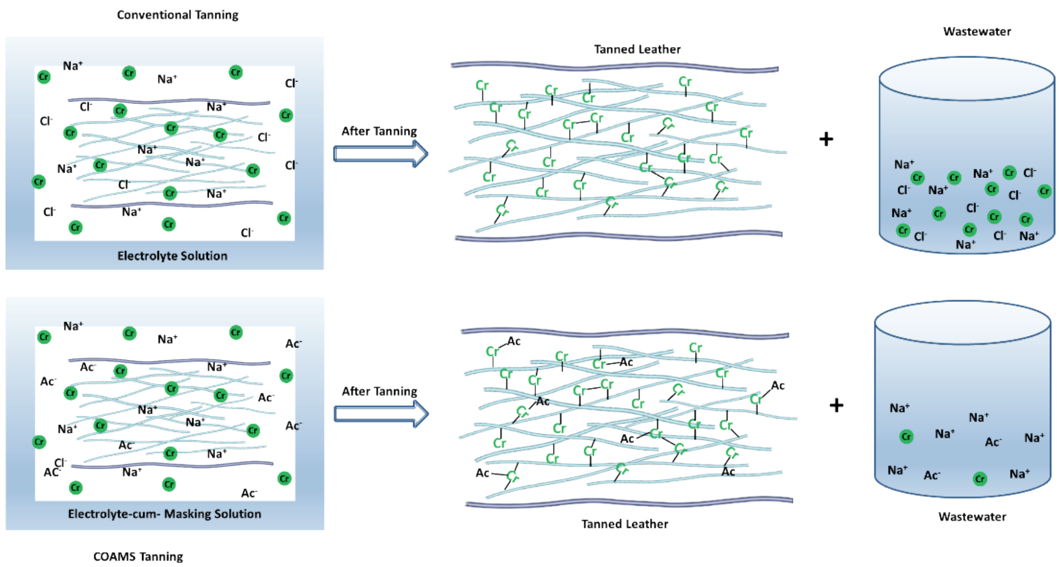

Figure 1. The possible Mechanism of COAMS Tanning System

is to only alter the charge/hydrolytic behavior of chromium and also to increase the precipitation point of chromium. In this approach, the masking salts are added before acidification process in order to prevent the acid shock as well as to modify the nature of BCS which results in enhanced diffusion. The delimed pelts have been treated with sodium acetate for 30 minutes followed by acetic acid treatment. During the acetic acid treatment surface pH of the pelts was buffered around 5.5 and its closer to the IEP of hide matrix (4.7). It is well reported that the hide/skin matrix undergoes minimum swelling when the pH is near the IEP. Therefore, the buffering action created in the system may prevent the acid shock during the sulfuric acid addition. Besides, masking salts added into the system act as electrolytes which would reduce the ionic imbalance when the protein amino group undergoes protonation during acidification process. As a result, the combined effect of buffering action and reduction in ionic imbalance would help to reduce the pH without acid swelling in the absence of sodium chloride. The mechanism of the developed approach is pictorially shown in Figure 1. During the tanning process, acetate anion exchanges the water ligand in co-ordination sphere and permanently attaches to protein-chromium complex and acts as electrolyte during acidification. In this method, the float volume has been reduced to 50%, in order to increase the ionic strength and concentration gradient. Shrinkage temperature of the wet-blue leather was found to be 104°C and the chromium exhaustion was 90%.

Microscopic Analysis

The wet-blue leathers obtained from two different tanning systems and its matched pair control leathers were analyzed through Celestron handheld microscope. The surface and cross-sectional microscopic images of CTDL and COAMS system are shown in Figures 2 and 3, respectively. It has been observed from Figure 2 that the surface of the CTDL leather is flatter than control leather and fiber bundles are compact in nature. The surface micrographs

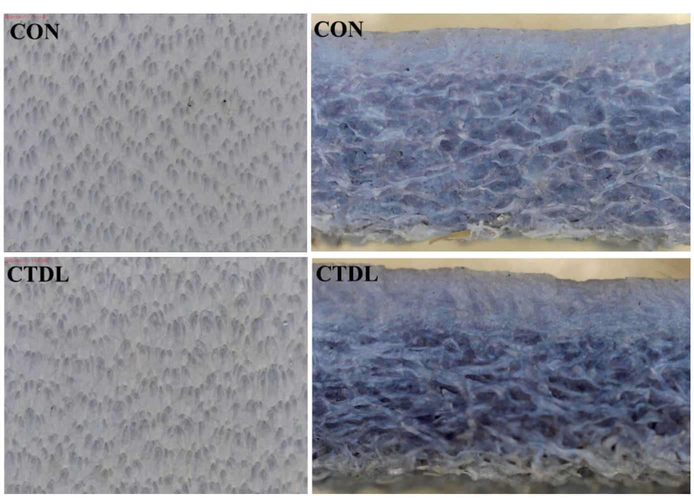

Figure 2. The surface and cross-sectional view of wet-blue leather of matched pair control and CTDL process

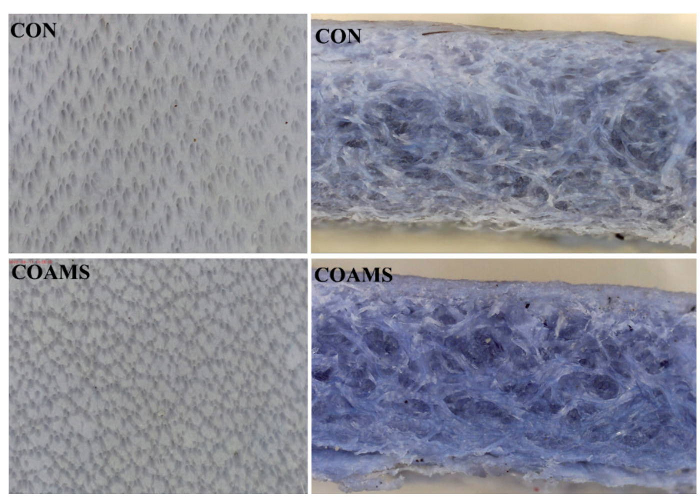

Figure 3. The surface and cross-sectional view of wet-blue leather of matched pair control and COAMS process

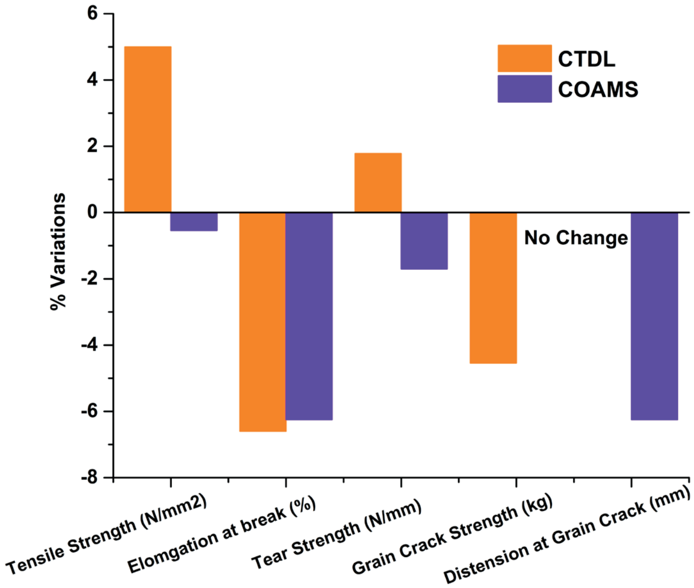

Figure 4. % Variations in physical strength characteristics of leather processed from pickle-free tanning system with respect to conventional process

of COAMS shows well dispersed and finer hair pores than control leather (Figure 3). It is also evident from cross-sectional view (Figure 3) that fiber bundles are slightly darker blue in nature which may be due the masking effect of acetate used in the tanning process.

Physical Strength Characteristics and Organoleptic Properties

Wet-blue leathers obtained from experimental processes and its matched pair control leathers were further processed into crust leather. The effect of new tanning system on mechanical properties of final leather were analyzed and the variations in strength characteristics with respect to control leather are shown in Figure 4. It is evident from Figure 4 that the tensile strength of CTDL leather increased about 5% whereas it is marginally reduced for COAMS leather. It is also observed that both CTDL and COMS leather exhibits lesser elongation than the control leather. The grain crack strength of CTDL leather is reduced and no difference has been observed for COAMS leather. Whereas no change in distension at grain crack for CTDL leather and around 6% reduction has been observed for COAMS leather.

Organoleptic properties of the crust leathers were examined by experienced personal and rated on a scale of 1-10. Grain tightness, roundness and fullness of the CTDL/COMAS leathers are superior (9/10) to that of conventional leather (8/10). However, softness of the control leather (8.5/10) is superior to that of CTDL/COMAS (8/10) leather.

Analysis of Wastewater

The composite wastewater (Deliming to Tanning) collected from each process was analyzed for various pollution parameters and the results are given in Table V. It is evident from Table V that the conventional process generates 3.72 m^3 of wastewater for each metric ton of raw materials whereas it is 0.4 m^3 and 2.7 m^3 for CTDL and COAMS process, respectively.

The developed processes enjoy enormous reduction in TDS load. The TDS load discharged from conventional process is 151 kg/ton whereas it is reduced to 35 kg/ton and 43.5 kg/ton for CTDL and COAMS process, respectively. Besides, the uptake of chromium in pickle-free processes is around 90% whereas it is only about 67% in conventional process. The photograph of the wastewater collected from different tanning systems is shown in Figure 5. It is clear from the Figure 5 that the conventional liquor is darker than other two tanning system.

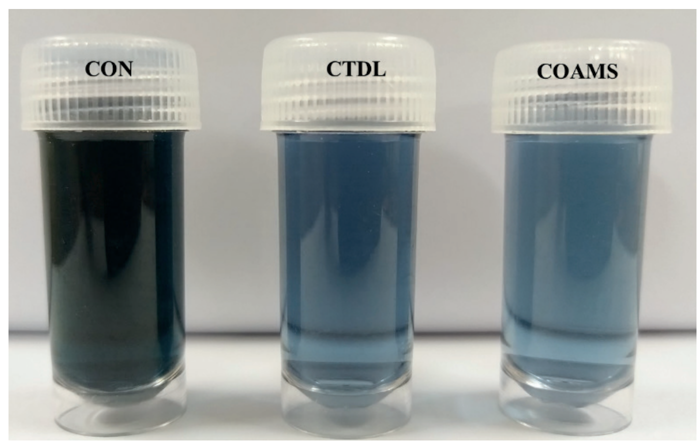

Figure 5. Spent chromium liquor from conventional and developed salt-free tanning system

Table V

Characteristics of wastewater (Deliming to Tanning)

Parameters	CON	CTDL	COAMS
Volume of wastewater (m^3/ton)	3.72	0.4	2.7
TDS load (kg/ton)	151	35	43.5
Cr_2O_3 load (kg/ton)	6.1	1.26	1.06
BCS offer (%)	8	6	6
Chromium Exhaustion (%)	67	90	92

Conclusion

In the present work, two different approaches have been developed for high-performance pickle free chrome tanning process. The developed methodologies can be adopted for all kinds of raw materials and any type of tannery. The methodologies have been developed in such way that only common chemicals which are normally used in leather processing are employed. The developed processes completely avoid the usage of sodium chloride and alkali for basification process. Hence, the developed methodologies are economically beneficial and environmentally sustainable. The salient features of the developed system are given below.

1. Suitable for all kind of raw materials
2. Complete elimination of salt usage and basification process
3. Chromium exhaustion: >90%
4. 71-77% reduction in TDS load (deliming to tanning)
5. Reduction in BCS input
6. Significant reduction in water consumption
7. The obtained leathers are fuller and tighter

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Improving Tearing Resistance of Leather - Part 2
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.

The aim of this work, divided in Part 1 and 2, 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. Part 1 has been published in *JALCA*, 116(12), 2021.

6.0 Deliming

During the deliming operation, there is a lowering of the pH and extraction of adsorbed and combined $Ca(OH)_2$. There are numerous deliming agents and systems that, properly conducted, do not compromise physical properties.

As a consequence of the pH changes, the hides suffer a significant degree of deswelling.

It should be considered that high temperatures, above 30°C, are harmful to fibers because of collagen hydrolysis at this stage.

7.0 Bating

The use of enzymes at this stage, breaking down non-structural proteins, loosening and removing scud, slackening the hides and improving the elasticity and smoothness of the grain, deserves attention.

Bating agents are mainly from several origins: pancreatic, bacterial, fungal. The active content of bates are blends of enzymes designed to give particular effects. Even though collagen is resistant to general proteolytic enzyme activity, damaged-collagen because of scratches or insect bites, fresh or unhealed, delay in soaking or curing or alkali-damage, can be attacked by general proteases and be degraded. That is why enzymatic processes must be careful controlled, for prolonged action, overdoses, temperature increase and details as uniform distribution of enzymes in vessels.

Never keep bated hides in stock even if washed, remaining bates inside keep working.

In summary, bating should be a short time process, lots with extended standard timing, label them as RISKY.

Visual and manual evaluation of bated hides is very important since up till now there is not an objective method for industrial control.

It is worth mentioning that in comparative production trials in an upholstery tannery, increasing 10 times the % of normal bating enzymes keeping the bating time fixed, it was found that the average tearing strength increased by 10%. This could be explained because of the loosening of hides' structure that allowed better fiber movement and alignment to resist tearing forces.

8.0 Pickling

Although the pH lowering of bated hides with acids in presence of sodium chloride to prevent acid swelling seems very simple, it is a complex and dangerous step regarding physical properties in general and tear strength in particular.

We all have learned about the destructive effect that swelling can have on collagen, being the acid swelling the most dangerous one. Even if swelling is supposedly under control, acid hydrolysis takes place due to the increasing temperature resulting from the drum mechanical action.

Figure 10 illustrates the drastic effect that increasing temperature has on hide substance hydrolyzation, via Belavsky.[28]

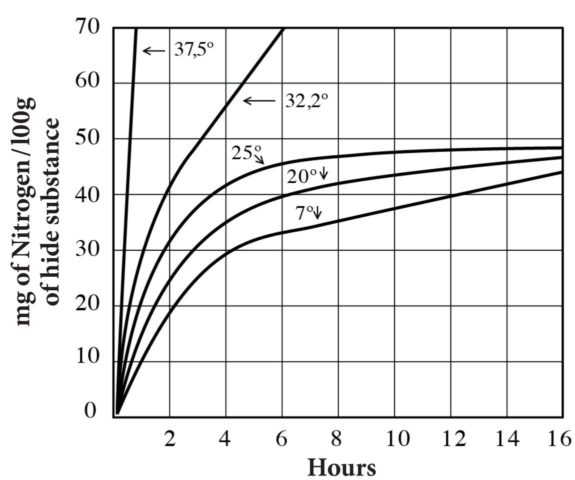

Figure 10. Pickle duration and temperature effect, on hide substance hydrolyzation[28]

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Given the complexity and dangers of the variables, the following factors must be taken into account to have this process under control and avoid irregularities as much as possible. Irregularities that otherwise will be reflected in tearing abnormalities.

- Pickle results will depend on the degree of deliming, mainly in full substance hides.
- Float percent and drum rotation must be such that the increase of drumming temperature be as low as possible.
- Low rotation peg drums have the disadvantage of producing low mixing action, and if liquid products are added through the hollow axle, it will take them too long to arrive to the other side of the drum. In the meantime, part of the hides will be subjected to a higher concentration of products decreasing down to equilibrium, while another part will be subjected to a zero concentration up to equilibrium. The result is that the batch of skins will not be uniform. Better mixing action at low rotation speed can be obtained with drums with deep shelves.
- Cooling hides with ice cubes before starting pickle is a good practice. For instance, starting the process at 15°C and not going over 18°C at the end.
- Start with a small % of NaCl to drained hides and allow salt be taken up to prevent acid swelling. Complete the float with a mixture of brine that fits the requirements with sulfuric acid cooled down overnight, is also a good practice.
- To totally avoid the use of sulfuric acid in the pickle is a much better practice. Not only because the danger of personal or environmental accidents, but also because dosage mistakes can be the cause of physical properties irregularities very difficult to trace back and assign later on.

8.1 Tear strength loss estimate

Since the authors could not find in the literature a direct relation between tearing strength variation with pickle temperature, there is one presented here.

The following test was carried out in a tannery working with traditional pickle.

One lot of limed and split hides was divided in two and processed in two tanning drums.

One drum with normal pickle that ended normally with 28°C after 4 hr. running. In the other drum, hides were cooled down as well as the float water in such a way that after 4 hr. running the pickle ended at 23°C.

The rest of the tanning process was done in the standard way up to wet blue state.

Table II

	Means N/mm	STDEV
Normal 28 °C	29.8	8
Trial 23 °C	33.1	6.4

The hides were identified, shaved, mixed and followed standard process up to crust state where they were sampled for tear test IUP 8, 40 samples for each trial. Results are shown in Table II

The two means are significantly different with P = 0.045

It is interesting to observe that not only the strength at 23°C is higher but the standard deviation is lower.

Now these results can be associated with the data of Figure 10 to find a relation between tearing strength variation and pickle temperature.

Extrapolating values from Figure 10 for 4 hr running time and 18, 23, 28 and 32°C, the loss of hide substance at these temperatures can be estimated.

With these figures and tannery data of Table II, the behavior of leather tearing strength with pickle temperature is estimated as shown in Figure 11.

Taking 28°C as the basis of calculation, the tannery found that going from 28° to 23°C increased the tear strength from 29.8 to 33.1 that is 3.3 N/mm.

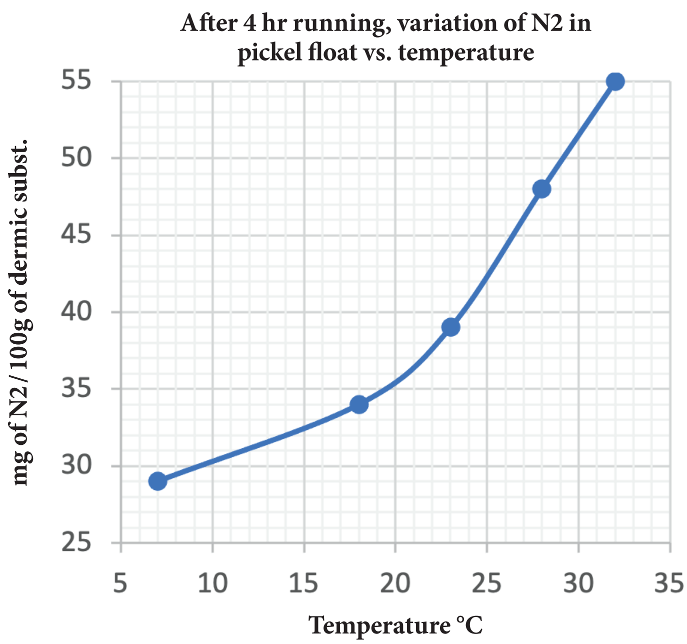

Figure 11. Variation of hide substance in pickle float vs. Temperature, with 4 hr running time

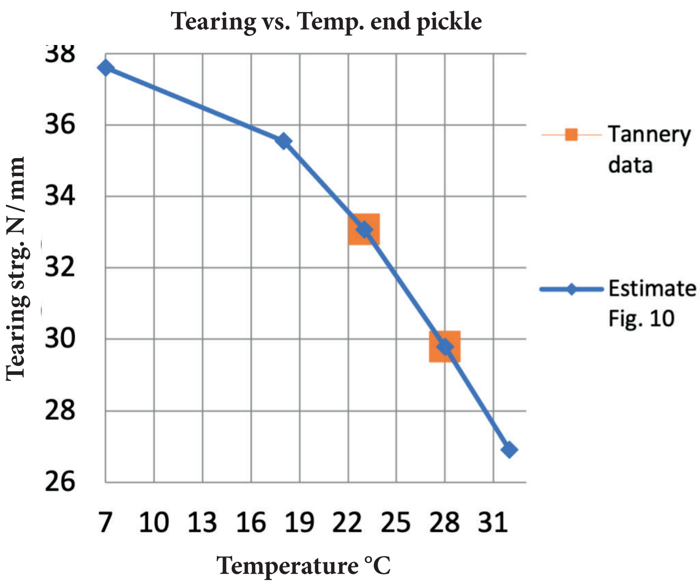

Figure 12. Tearing strength variation vs. end pickle temperature

From Figure 11, going from 28°C (48 mg of N_2) to 23°C (29 mg of N_2) 9 mg of N_2 were saved meaning that each unit of dermic substance equals 0.41 N/mm.

With these data the following graph is made.

Figure 12 shows the dramatic influence of temperature variations on tearing in traditional pickle.

Despite its strong influence, this factor was generally underestimated.

This illustrates that, in order not to damage the collagen fibers, work must be done with non-swelling acids and other auxiliaries or try new no-pickling chrome tanning systems.

Nowadays there are numerous proposals using different chemical products and systems to achieve this.

In any case, the suggestion is to test any of the commercial proposals on the tannery floor, with the sequential sampling method employed by Tournier,[9] to confirm the collagen non-altering effect of the product or system used.

9.0 Chrome tanning

Although there are many references about the influence of chrome tanning itself on tear strength[20] not all of them are coincident whether it increases or decreases tear strength. There are divergences among different researchers and there is not a consensus.

Under our leather technologist experience, we adhere to the branch that states that chrome tannage itself decreases in some degree tearing resistance and can extend it to vegetable tanning.

Bienkiewicz, 1983,[21] is very clear with the concept that with the introduction of tanning agents into the hide, some "dilution" effect of native collagen properties could be expected. Also, Lollar[29] states clearly that "…the tanned fiber is weaker than the untanned fiber."

What else can be said about chrome tanning itself?

- That the chrome distribution must be as uniform as possible through the leather thickness
- The total chrome content, pH, differential pH, ash, humidity and grease content, must be within reasonable limits lot by lot
- Good mold development resistance
- Color uniformity and absence of stains

At least, all these parameters must be agreed upon between buyer and seller when commercializing wet blue.

It could happen that in the future, when buying and selling split or shaved wet blue, the wet tearing strength would be included as a requirement.

10.0 How to select stronger hides

In the Introduction it was said that tanneries apply heavy weight hides to produce low substances articles, compromising physical properties.

Later on, it was explained that collagen fibers in the corium layer of a hide or skin give leather its strength; the grain layer on its own is relatively weak. Consequently, if an excessive quantity of corium is removed by splitting and shaving, the leather will become weaker, as shown by Covington.[1] The grain to corium ratio should be lower than 50%.

Also, it is generally known that strong leathers show thinner grain layer than weak ones.

In Section 1.7 we cited Dr. Haines stating that physical properties are more a function of original hide thickness than breed or age of slaughter. A direct conclusion is: in order to produce thin leather, select thin hides.

The question is: How could all this information be translated to the tannery floor in a practical way?

In order to find a non-theoretical method to select stronger hides for demanding leather articles, the following assay was conducted in a tannery.

At the exit of a full substance wet blue hide sammying machine, equipped with a continuous substance measuring device, the hides were selected according to the thickness in the kidney area.

Hides were classified in following ranges:

Range I: < 4 mm, number of whole hides 42

Range II: 4.1-5, 42

Range III: 5.1-6, 27

Range IV: 6.1-7, 23

Range V: > 7 mm, 2 whole hides

Totaling 136 whole hides.

All hides were marked for range traceability, split to 1.7 mm, shaved to 1.3 mm, cut in sides and processed up to crust for shoe upper leather.

Finally, the 272 sides were sampled in the official area, parallel direction only, tested for continuous tear with ALCA method E 10 (trouser tear) and expressed results in Newtons.

The following graph, Figure 13, shows the results.

In this way we put numbers to Mrs. Haines and Covington statements and suggest a method to improve tearing strength in the tannery, selecting stronger hides.

For tanneries splitting in the lime, a continuous substance measuring device can be applied either at the exit of the lime fleshing or at the entrance of the splitting machine. Nowadays there are splitting machines in the market that measure thickness at the entrance of hides and automatic continuous programmed adjustments of splitting substance can be accomplished.

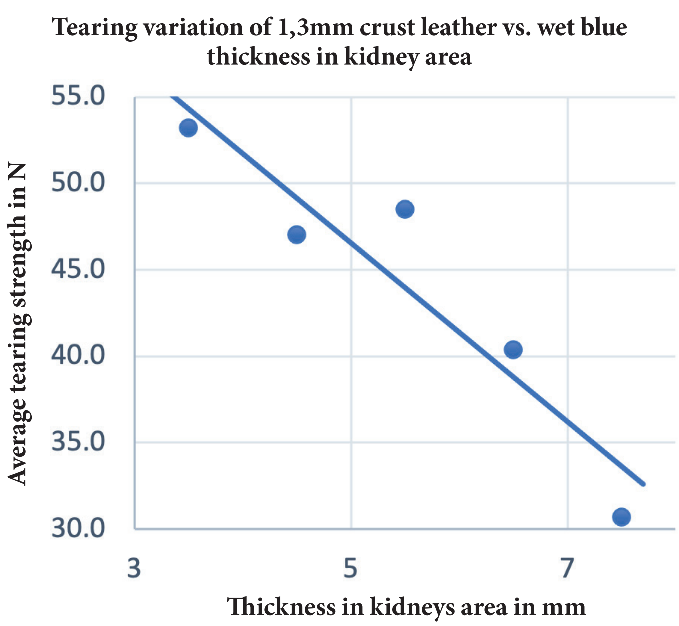

Figure 13. Relation between thickness in kidney area and tearing strength of crust leather.

11.0 Vessels and mechanical action

There are several vessel types: traditional drums, Y drums, paddles, mixers, washing machine types, etc.

If on top of these variety, different sizes, rotational speeds, internal additaments (pegs, shelves, etc.), loads, floats, times of processing, etc. are added, it happens that there are numerous variables and degrees of mechanical action.

The election and administration of these variables is handled discretionary by tannery technicians according to the equipment of each tannery, their expertise and results desired over leather.

Even though mechanical action promotes penetration, excessive mechanical action can produce not only grain abrasion but increase fiber disruption affecting tearing strength among other properties.

12.0 Post tanning operations

12.1 Neutralization

Mild and complete penetration of neutralization proved beneficial to tearing strength since it helps in the uniform distribution of subsequent products applied.

In particular, according to Altrock in 1995,[23] the use of sodium thiosulphate has been found beneficial for good tearing properties.

12.2 Retannage

Like the chrome tanning there are different opinions about if retannages increase, lower or not influence tear strength at all. Our position is to adhere again to the Bienkiewicz[21] concept, that with the introduction of tanning agents into the hide, it is right to expect some "dilution" effect of native collagen properties. Hence, a tendency to lower physical properties, depending of course on the type and quantity of products can be foresee.

Another important point to consider is the overall effect of retannages and fillers. They can increase the substance of original shaved leather or not influence it at all.

Here again, it depends on the type and quantity of products.

As a rule of thumb, if the retannage and filler increases the substance of a particular crust and to maintain the customer agreed substance, it is necessary to lower 0.1 mm the shaving substance, the average tearing strength of the lot will be lowered in 10% approximately.

In this case the quantity of low tearing values will increase and the risk of customer claim also increases. Instead, it is worth trying to lower the retannages and filler load and not to modify shaving substance.

12.3 Fatliquoring

The fatliquors are the only products that certainly improve tearing strength and other physical properties. Their function is to lubricate fibers and fibrils impeding them to re-stick when leather dries out, allowing them to slide over one another, once leather is dry at equilibrium humidity.

This sliding makes for flexibility and softens the leather and help fibers to align in the sense of the strain in any direction, as explained in point 1.2.

In 1953 Benskin,[22] studying several factors influencing tear and tensile strength found that tear strength increases rapidly from a zero-grease content to a maximum at about 10% grease, but subsequent increase does not add appreciably to the strength. He also found that a commercial upholstery leather with 11,5% grease, when degreased, the tear strength fell by over 31%.

Bitcover and Everett[23] in 1973, studying the separate influence of chrome and fat content on crust leather found an inverse correlation with chrome content and tear strength and a direct correlation between fat content and tear strength.

Personal experiences of the authors confirm this trend and can add the following comments:

After reaching the maximum tear, further increase of fatliquors tend to lower the strength.

In order to reach with fatliquors a complete penetration up to the finest components of the collagen structure, distribute them in multi-stage applications with smallest particle size emulsions.

Choose the appropriate fatliquors for each of these steps: pickle/tanning, neutralizing, retanning and main fatliquoring.

Play with the preparation of fatliquor emulsion, water in oil or oil in water, to find the method that gives the smallest particle size emulsions. And keep rutinary test tube samples of each main fatliquor emulsion prepared for each lot, to control the thickness of the cream formation, next day.

12.3.1 Mitigation of low tearing with oils

It can happen in any tannery that in a certain moment due to an alert from the control system or a customer complaint, we realize that the tear values are low. In the meantime, technicians start to investigate the possible cause, the problem can be mitigated for the leather in the pipeline by a modification of the main fatliquor, for instance.

Facing a real problem in a tannery and knowing that it is the neutral oil that is the real lubricant[1] we performed several pilot plant trials adding different percentages of raw winterized neatsfoot oil to the mixture of oils of the main fatliquor, comparing against the normal formulation for shoe upper. We used 8 wet blue hides shaved 1.5 mm for a shoe upper crust. The hides were halved and the sides properly marked. The 16 left and rights sides were processed together up to the end of retannage. Afterwards, three lots were prepared. Lot 1, with 8 sides, 4 lefts and 4 rights, and the 8 sister sides were put in Lot 3. Lot 2, with 8 sides, 4 lefts and 4 rights, and the sister sides went to Lot 3 totaling 16 sides.

According to the WB average side shaved weight, the fatliquor formula weight was calculated for each lot.

Lot 3 (16 sds.) normal fatliquor as blank, Lot 1 (8 sds.) normal fatliquor plus 0,5% of winterized neatsfoot oil and Lot 2 (8 sds.) normal, plus 1,0%. Drying and softening as usual.

Following graph in Figure 14 shows the results of tearing strength in N/mm of final crust.

The improvement in tear was obvious, but the additional oil started to affect negatively the article characteristics. With 1%, the softness was excessive producing a coarse and sugary grain and looseness in pockets, veins were more evident and somewhat excessive elongation.

In this particular case, technicians chose 0.6% to overcome the problem.

12.3.2 Mitigation of low tearing with moisture

Humidity is another factor influencing tear strength. Each leather article has different equilibrium moisture according to the ambient

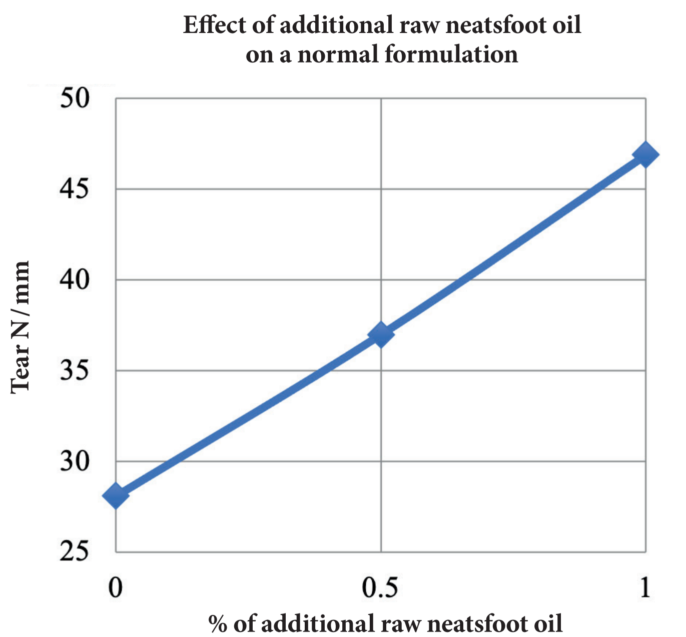

Figure 14. Effect of neatsfoot oil in tearing strength.

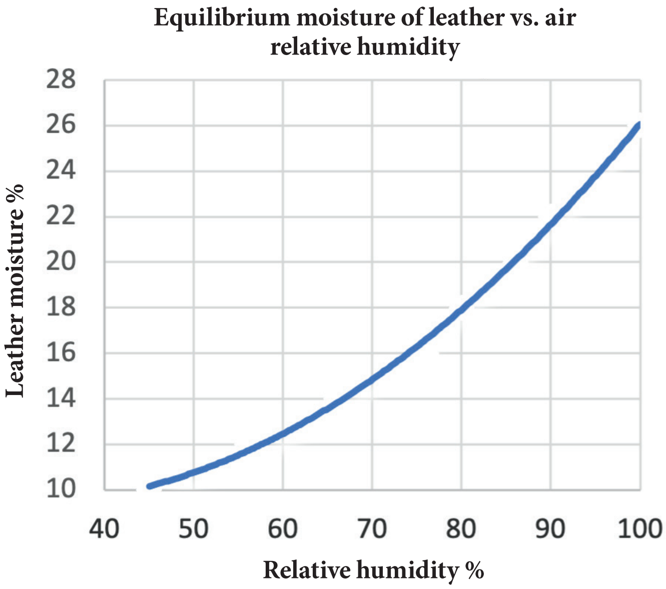

Figure 15. Equilibrium leather moisture vs. ambient humidity.

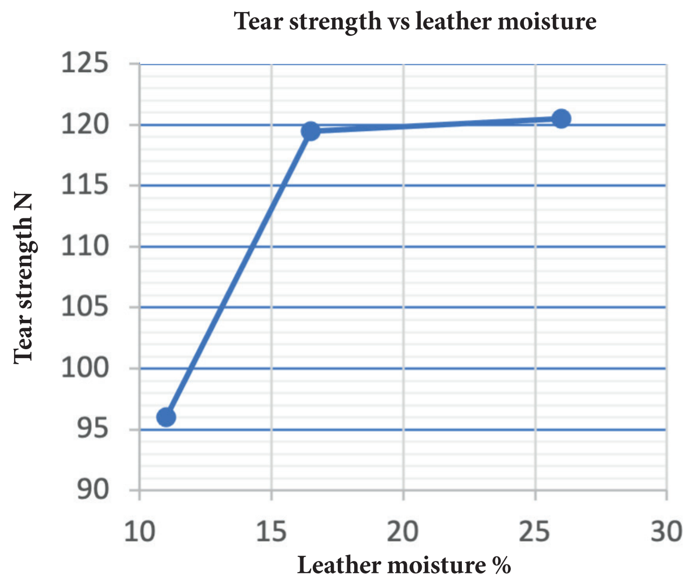

Figure 16. Evolution of tear resistance with leather moisture.

humidity where it is placed. In the following graph, Figure 15, is represented the general tendency to absorb humidity of finished leathers.

In order to see the influence of different leather moistures content in tear strength, we performed the following study.

We extracted official samples out of 50 sides of a shoe upper crust, 1.6/1.8 mm. Samples were cut for double edged (slit) tear resistance, IUP 8, perpendicular to backbone, 3 cuttings for each sample. So, there were 3 sets of 50 cuttings per set.

Each set was stored 48 hr in a hermetic chamber with different relative humidity at 25°C, namely: (1) water, (2) salts in water and (3) concentrated sulfuric acid. After each one of the 48 hr, leather moisture was measured with 2 methods, AquaBoy readings and drying to constant weight in an oven at 102 ±2°C, Table III

Finally, tear resistance was measured according to double edged slit method, IUP 8.

Table III

	Group		
	1	2	3
Humidity	**Low**	**Medium**	**High**
AquaBoy	6/8%	12/14%	22/24%
Oven	11%	16.5%	26%

Results are in the following graph of Figure 16

This means that:

- Leathers coming out of the tannery with low humidity should be avoided. Otherwise, moisturize finished leather. Not only to preserve physical properties, but also softness, area, substance, etc.
- Avoid leathers with more than 16% moisture because of danger of mold development in stock.
- Fatliquoring agents containing lanolin and other auxiliaries can regulate moisture content.
- Quite often, leathers coming out of the finishing room after suffering tunnel dryers, show moistures well below 10%. These leathers will have tear resistance 15% lower than the same with normal moisture. This strength loss can be recovered easily by moisturizing them.
- Inversely, leathers with border line strength at normal moisture, by means of moisturizing, can increase about 10% resistance.
- In some cases, it is possible to add an appropriate fatliquor to the moisturizing solution, to boost and lengthen the effect.

12.4 Drying and softening

This is another processing step that, if not well designed, standardized and controlled will affect leather quality, area yield, physical properties and hence, tearing resistance.

In this step, experience and expertise of tannery technicians are of utmost importance.

The evolution of the temperature gradient and the time in each dryer depend on too many factors to arrive to the desired article. Ideally the target is to obtain the desired moisture inside the leather at the end of the dryers that after a certain period of stocking time, for unifying the moisture, the lot reaches an adequate and uniform moisture to be subject to softening.

In general, it can be said that the softening moisture should be 18/24%. Lower than this can produce breaking of fibers during softening. Higher than 24% will force to dry again, to avoid the leather going to the next step developing mold and/or risking new stiffness.

Some comments and suggestions:

- The sammying operation previous to drying is justified since it is cheaper to eliminate water by pressing than by heating, but the lowest possible water content to be attained is about 55%, if higher pressure were to be applied the fiber structure starts to be destroyed, Heidemann.[24]
- Overheating in the dryers must be avoided since it can cause sticking of the fibers and even modify the inner structure of the fibrils. Both factors affect tear strength.
- Control differential pH of running production. Values higher than 0.7 indicate presence of strong acids, generally sulfuric. During drying, water evaporation produces the increase of concentration of acids present between fibers and fibrils with the corresponding increase of hydrolysis of collagen and destruction of them.
- Tension and toggle dryers must be dully controlled since drying normally produces shrinkage of leather adding extra tension that can break fibers and even tear the leather around toggles.

12.4.1 Vacuum drying

Even though there are several guidelines to work with each different type of dryers and their combinations, leather technicians use their experience, tradition and trial and error to adjust the drying and softening process for each article.

Regarding vacuum drying it is interesting to mention the work of Liu and DiMaio, 2001[25] about the correlation they found between the drying rate and tearing strength.

They defined the drying rate Ω as:

$$\Omega = (W_o - W_t)/(t)^{1/2}$$

where, W_o is the initial water content and W_t, residual water content at time t.

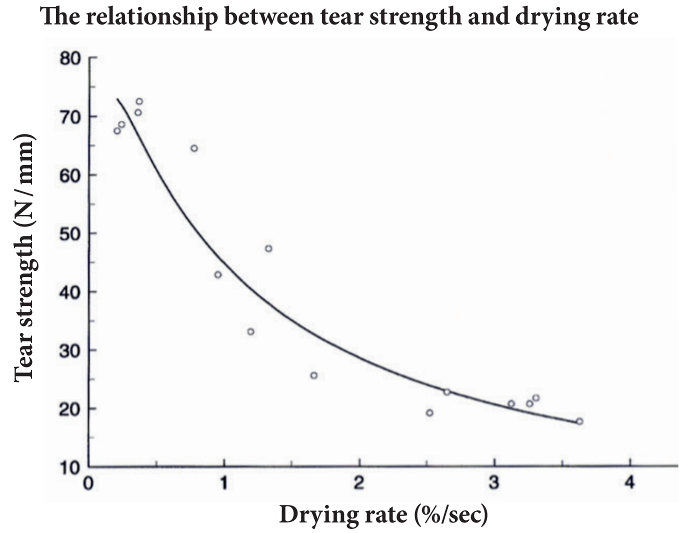

Figure 17. Tear strength vs. drying rate (With *JALCA* permission)

Figure 17, (Figure 5 in the original paper) demonstrated that tear strength correlates inversely with the drying rate.

According to the authors, their study has shown this newly defined drying rate dictates the resultant tear strength.

12.4.2 Softening

Staking and milling are the main mechanical operations to liberate fibers from adhesions between them during drying, that stiffen leather.

There is a direct interaction between fatliquoring, moisture, degree of softening and tear strength. This is another area where, to determine the perfect equilibrium among these and other factors for each article, requires a great amount of experience in the art of leather making.

Increasing softness increases the ability of fibers to align in the sense of the applied force, then, increases tear resistance.

But too much mechanical action starts to break fibers and lowers tear resistance.

Edmonds et al.[26] determined that, between unmilled and milled leather, there are average increases of about 4% in tear strength expressed as N and N/mm, about 8% in thickness and about 50% in softness (BLC Softymeter).

12.6 Finishing

Although the finishing operations affect mainly the surface of leather, there are some steps that have important influence in the physical properties and in particular, tear strength.

The application of different types of coats with different type of machines, imply the humidification of leather with subsequent dehumidification through drying tunnels.

The tunnels are designed to dry as fast as possible and generally over dry leather.

The ideal finishing tunnel, in our concept, is the infrared heated, but even in this case, the over drying exists in practice.

This over drying produces hardening of leather that must be corrected by additional softening, risking lowering tear resistance.

This hardening effect is critical when it comes to impregnations.

Additional heating and hardening is produced with embossing and plating.

The general picture at the end of the finishing lines is that leathers come out with very low moisture, well below 10-14% that should be the normal.

Sending this leather to customer, the tannery is risking several dangers, namely:

- Losing about 3% area yield, Figure 18 illustrates it.
- Claim if customer click templates, the component pieces are stacked in a humid environment, they absorb humidity, and change shape and size.
- Low tear strength according to discussed in 12.3.2 and Figure 16.

To correct this situation, leathers must be humected with water and some auxiliaries, by means of roller coating machines or spraying machines taking care of not to damage the grain side, or by hanging in humidifying rooms or tunnels set to 65-70% of relative humidity, see Figure 15.

The ideal situation would be to maintain the equilibrium moisture of the leather along the finishing room.

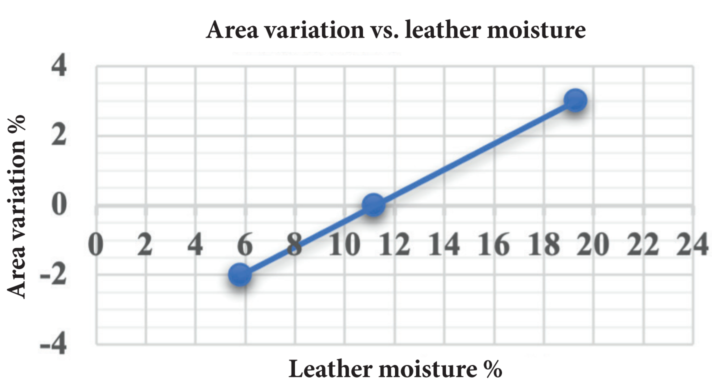

Figure 18. Area yield vs. leather moisture

Figure 19. Digital Scale with Hook

13.0 Final sampling

Generally, all lots ready for shipment are tested to check that they are up to standard for each customer.

In this sense, the work of Azzato and Tournier, 2019,[27] regarding the selection of a sampling plan to have sufficient protection not to send problems to customers, produces results of interest. They evaluate the different possibilities taking as working example the tear resistance of ten lots of the same article, of approximately 100 pieces each. The lots were 100% sampled in the official sampling area and tested with IUP 8 standard method.

13.1 Tearing, field manual testing

There are situations when it is necessary to check lots 100% to segregate substandard pieces with low tear strength.

This work is possible to perform by means of one of the numerous manually digital scales in the market, as the one in Figure 19.

A possible procedure is to make one or two incisions of 4 or 5 cm in the area of the official sampling, parallel to backbone, place the hook of meter and pull in the same way it does the lab dynamometer performing IUP 8 method.

It resembles the standard method by tearing a double edge slit.

In this way it is possible to segregate weak pieces that later can be checked out with the standard method in the laboratory.

14.0 Artificial improvement of tearing

From long ago, there have been attempts to increase leather strength, tearing in particular, by means of deposition of different polymers within the leather structure.

Vinylic, acrylic, polyurethane and other compounds are being studied.

Although there have been some successful applications, the leather treated in this way changes to a great extent the desired characteristics of normal leather.

Therefore, preservation and care of native collagen properties is the utmost objective of this paper and should be the same for leather technicians.

Conclusions

As seen along this paper there are many steps to take care of collagen fibers, that confer the strength to leather.

Among them, one of the most important ones are the steps between the flaying and the soaking that starts the leather processing.

The utmost care taken, protecting the original collagen fibers from degradation, not only will give good physical and subjective properties but high standard production level and yield. Also, the constant monitoring of different variables and quality, and the fine tuning of them, contribute to the final success of customer satisfaction.

It is our hope that some of the topics covered in this paper will serve as motivation and inspiration to the scientific leather community to deeply study them with the scientific rigor they deserve.

Acknowledgements

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