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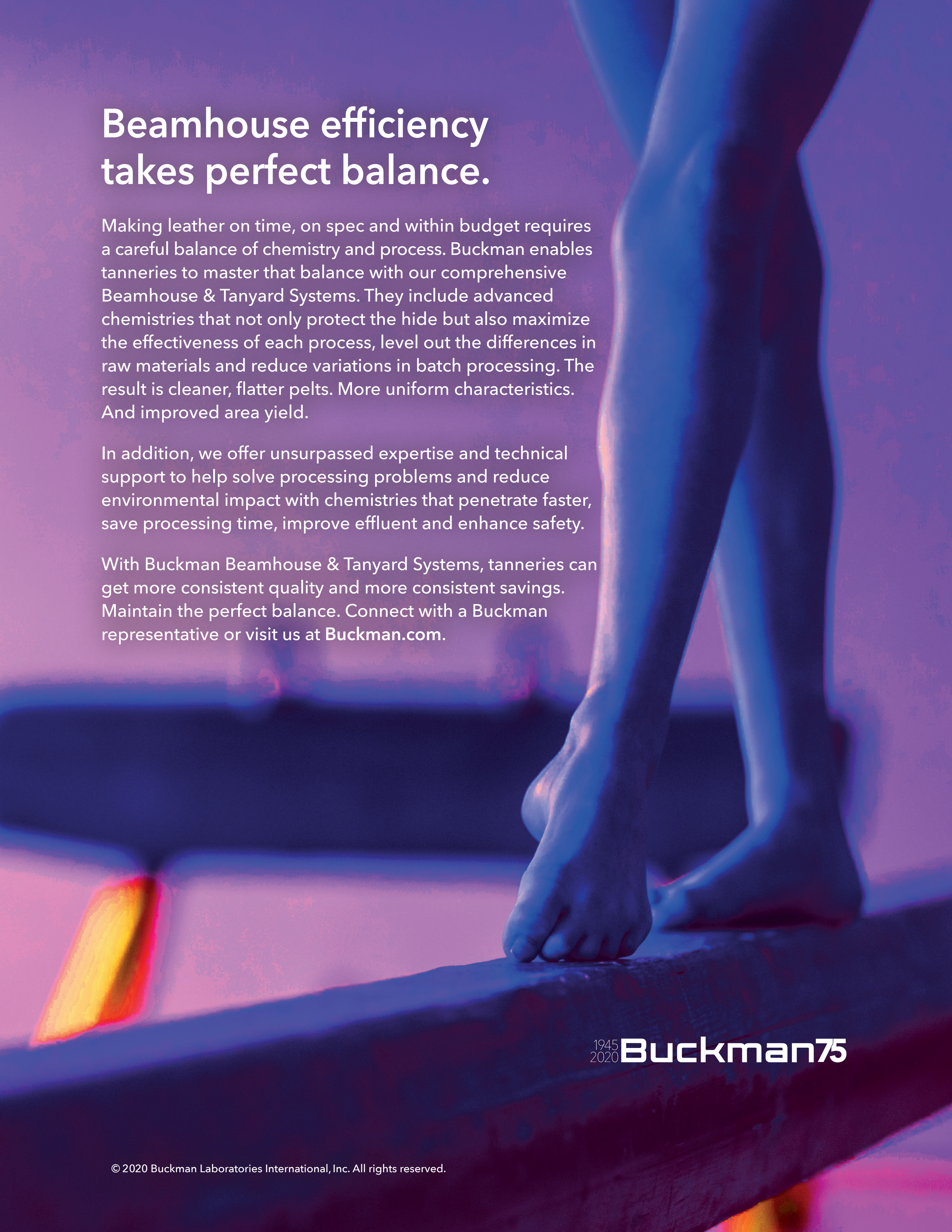
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JOURNAL OF THE

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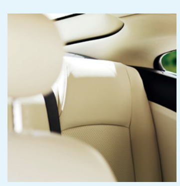

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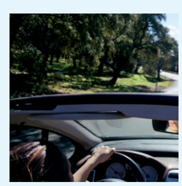

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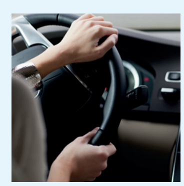

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Salt-free Chromium Tanning: Practical Approaches

by
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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)

Raw material: Cow limed pelts, Thickness (Neck): 8-10 mm			
Process/Chemicals	**% Offer**	**Time**	**Remarks**
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)

Raw material: Cow limed pelts, Thickness (Neck): 8-10 mm			
Process/Chemicals	**% Offer**	**Time**	**Remarks**
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

Raw material: Cow limed pelts, Thickness (Neck): 8-10 mm

Process/Chemicals	% Offer	Time	Remarks
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

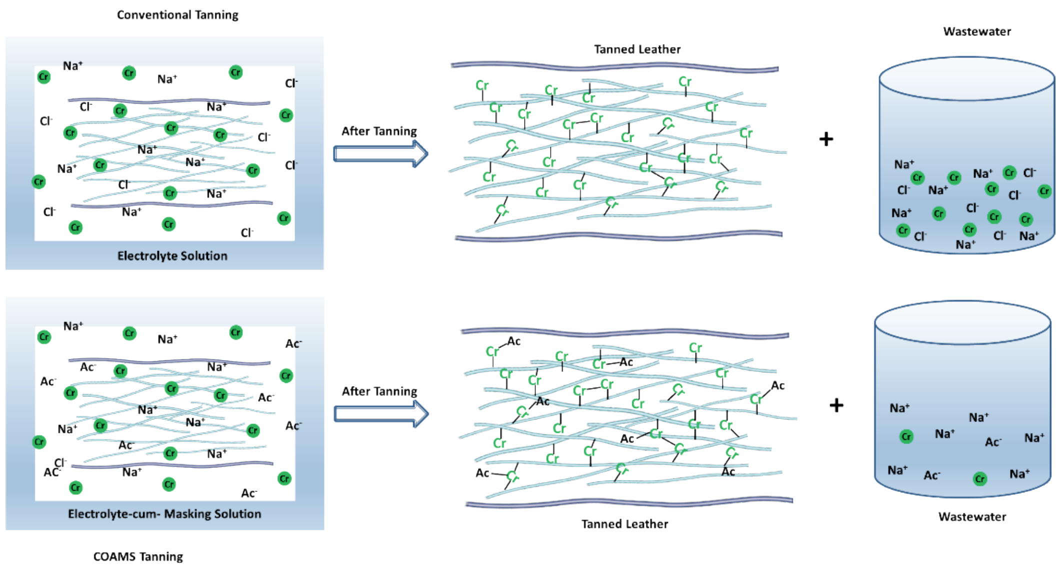

Figure 1. The possible Mechanism of COAMS Tanning System

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

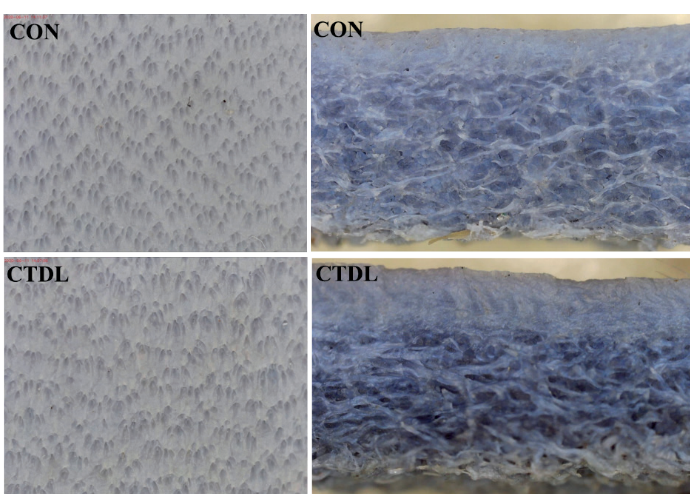

Figure 2. The surface and cross-sectional view of wet-blue leather of matched pair control and CTDL process

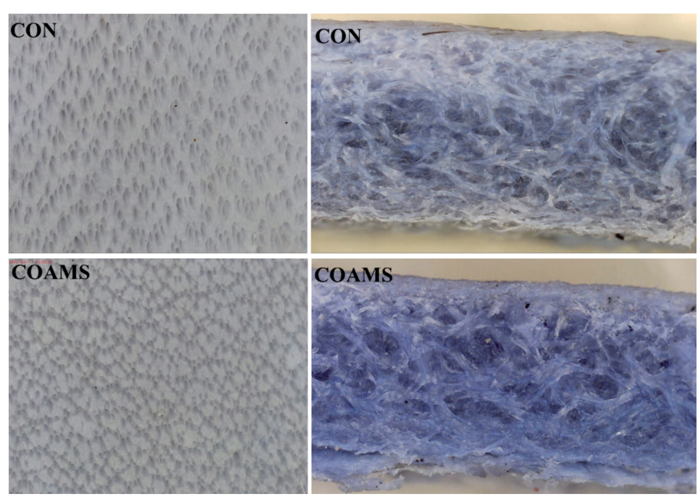

Figure 3. The surface and cross-sectional view of wet-blue leather of matched pair control and COAMS process

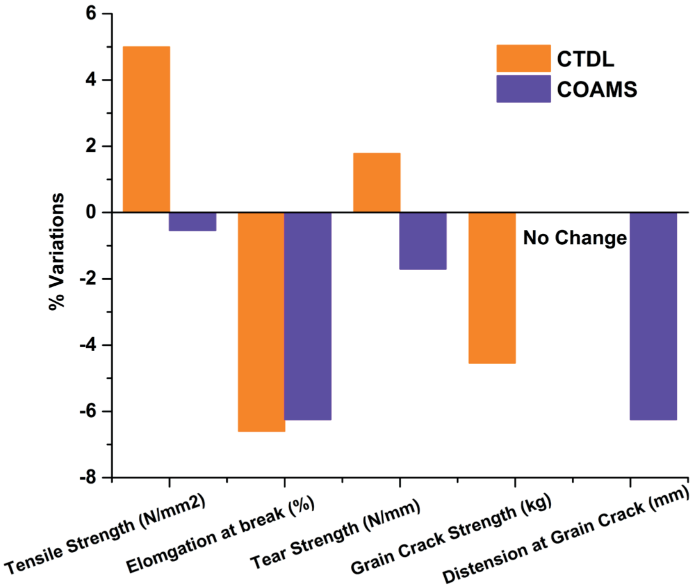

Figure 4. % Variations in physical strength characteristics of leather processed from pickle-free tanning system with respect to conventional process

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.

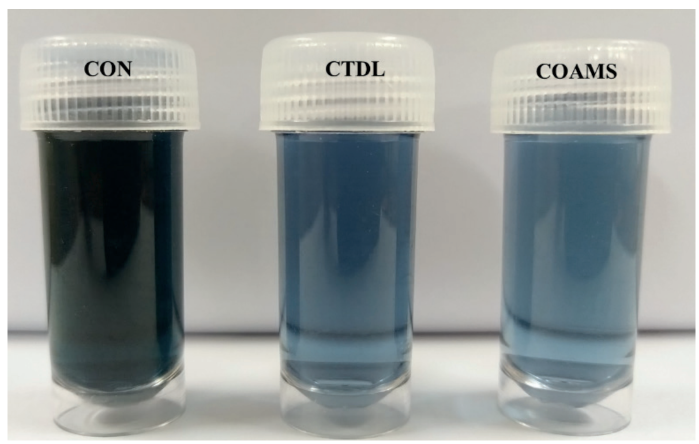

Figure 5. Spent chromium liquor from conventional and developed salt-free tanning system

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

Ricardo Tournier* and Fernando Lado

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]

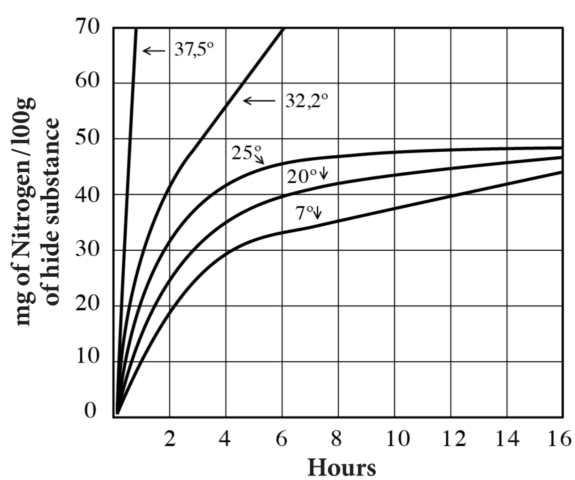

Figure 10. Pickle duration and temperature effect, on hide substance hydrolyzation[28]

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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.

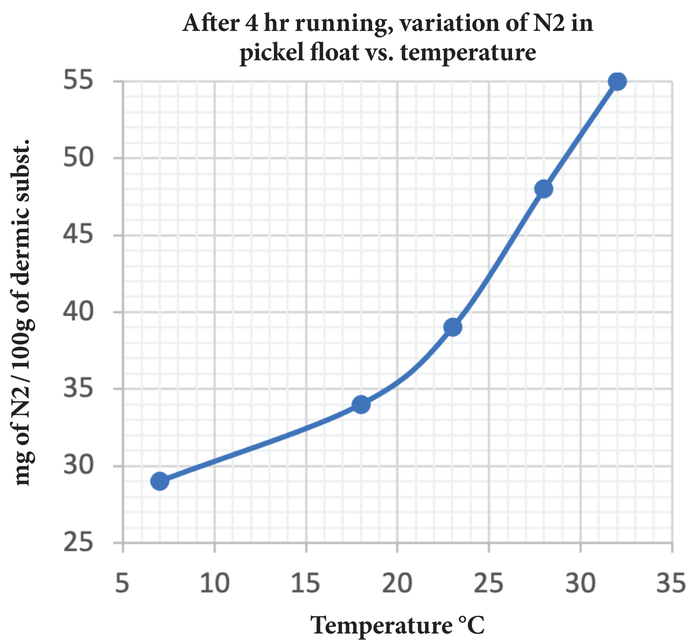

Figure 11. Variation of hide substance in pickle float vs. Temperature, with 4 hr running time

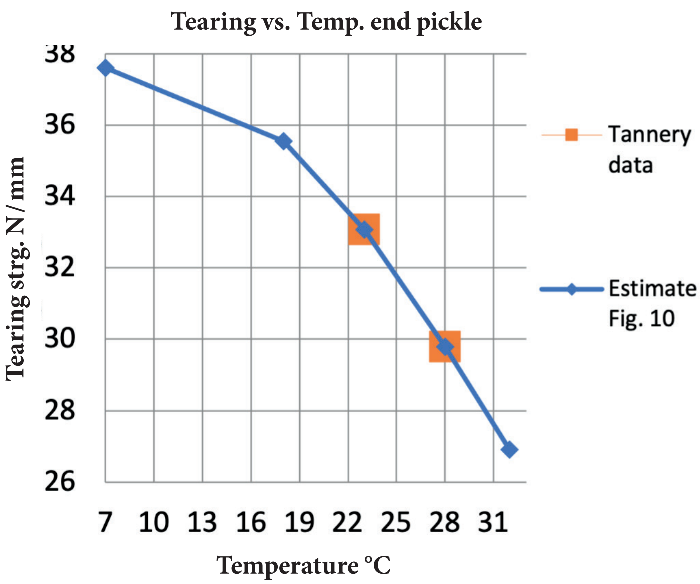

Figure 12. Tearing strength variation vs. end pickle temperature

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.

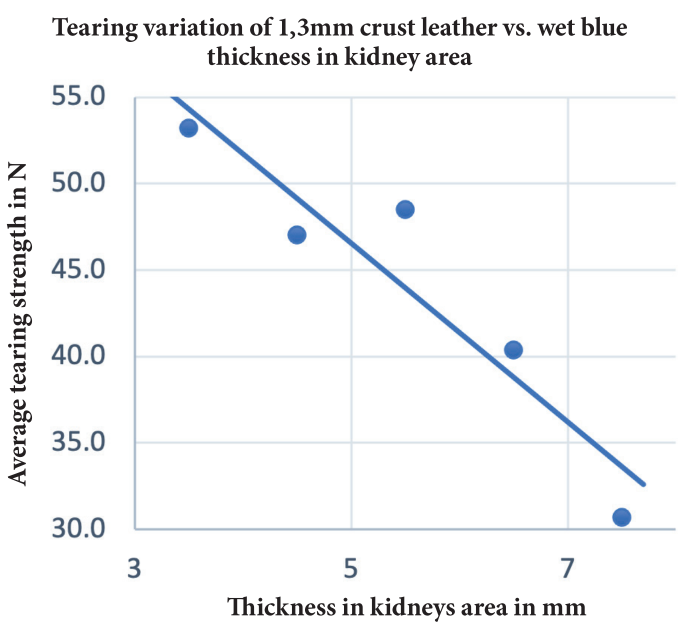

Figure 13. Relation between thickness in kidney area and tearing strength of crust leather.

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

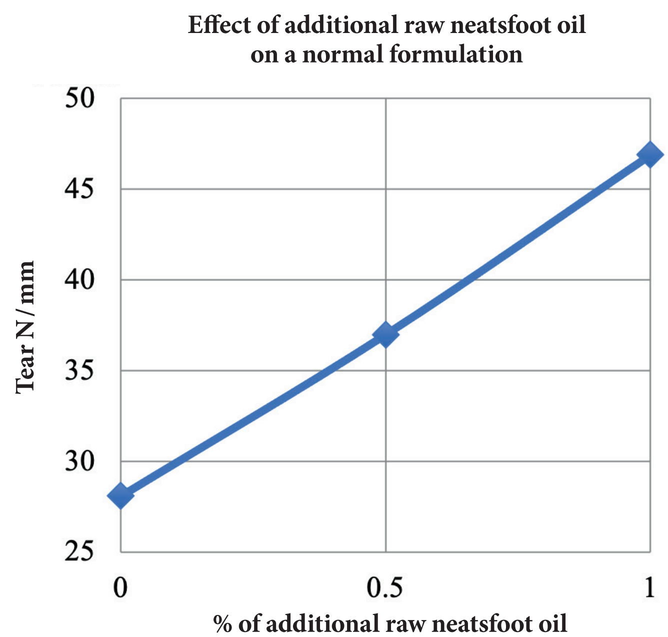

Figure 14. Effect of neatsfoot oil in tearing strength.

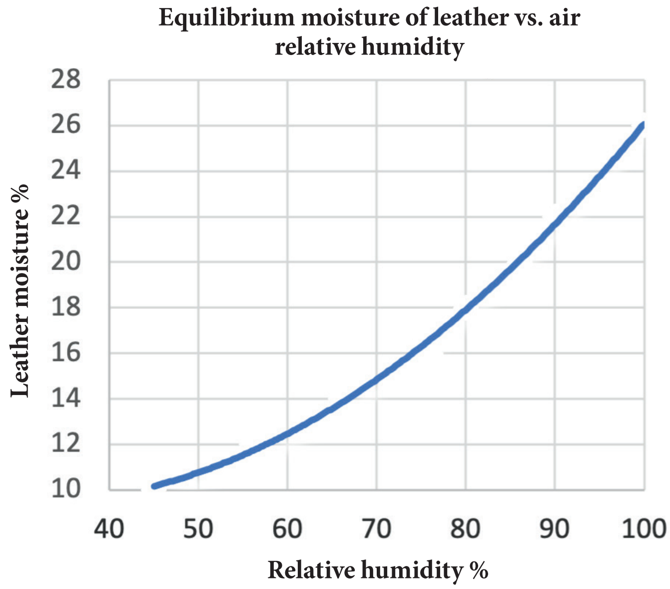

Figure 15. Equilibrium leather moisture vs. ambient humidity.

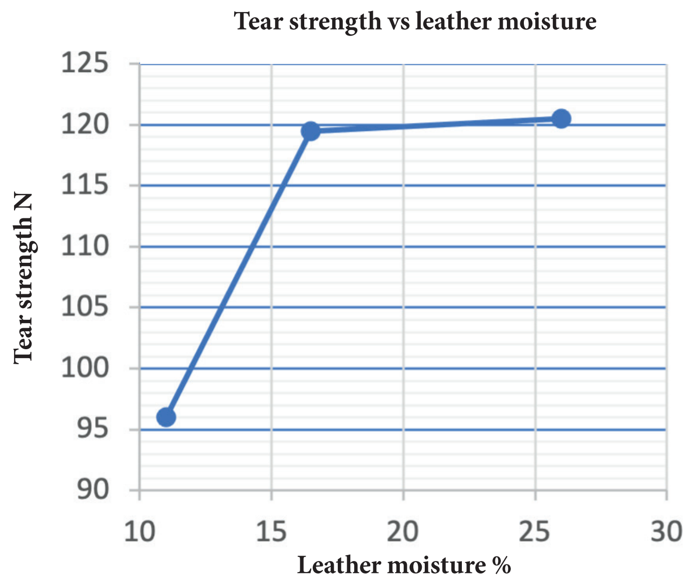

Figure 16. Evolution of tear resistance with leather moisture.

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.

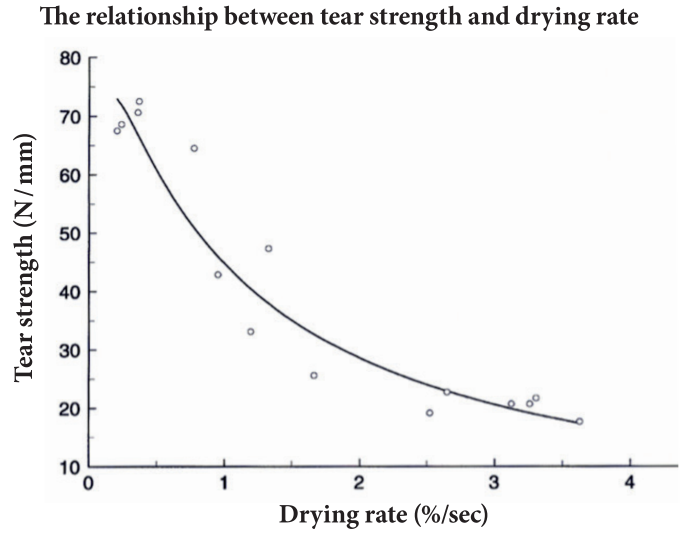

Figure 17. Tear strength vs. drying rate (With *JALCA* permission)

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.

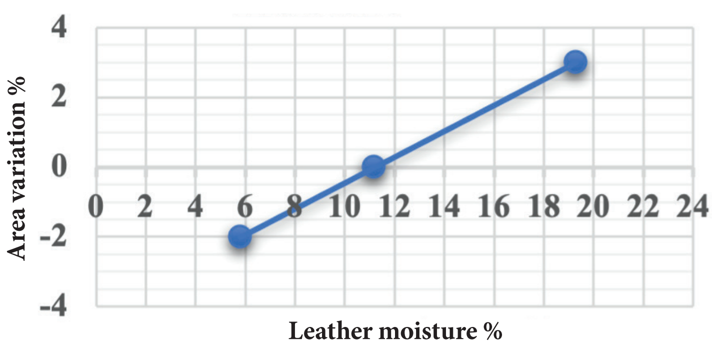

Figure 18. Area yield vs. leather moisture

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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A Cleaner Process for Short-Term Preservation of Hides using Wheat Bran

by

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Abstract

Salting is the most common method to preserve hides and skins. However, this preservation system requires the generation of large amounts of contaminated salt, approximately three million tons per year. In recent years several researchers have suggested different methods for the short-term preservation of hides using plant-based formulations, which either minimize or even completely eliminate the use of salt in the process. In this work, the possibility of using wheat bran for this purpose was studied. Two methods of application (dry and aqueous solution) have been developed. They enable the preservation of hides for one month, reducing by half the salt used in the preservation stage without undermining the quality of the final leather. These two methods contribute to the improvement of the overall sustainability of the tanning process.

With dry application, the use of salt is avoided and preservation occurs because the hide is dried. The application in aqueous solution (10% wheat bran) requires its previous hydrolysis and a minimum amount of salt (10°Bé). The preservation occurs because the acidity of the hide is increased.

Introduction

Hides are the raw material used to manufacture leather. In turn, leather is used to create a wide range of diverse objects including shoes, garments, bags, and saddles. The process to transform hide into leather is called tanning. Basically, the process consists in chemically stabilizing the collagen protein, which is the main component of the hide. This stabilization is achieved by incorporating certain chemical products, such as basic chromium salts, which react with collagen forming complex structures into the hide. The stabilization transforms the hide (which is an easily degradable material due to bacterial attack) into leather, a stable and useful material to manufacture multiple objects. To prevent hides from putrefying in the time gap between the animal death and the tanning itself, it is necessary for them to undergo a preservation process.[1-3] The most widely used method is salt preservation,[4] which dehydrates the skin and prevents bacterial growth. An annual expenditure of at least 3 million tons of salt used to preserve hides has been estimated.[5] It must be pointed out that the salt being used throughout the whole process is not reusable, which raises serious environmental and economic concerns.

Salt-induced soil degradation is a serious threat to global agro-ecosystems.[6] Salt as a waste from different industrial processes cannot be indiscriminately discharged into the environment. The solid salt used in the preservation and also recovered in solid form contains bacteria, fat, dirt, among other elements. Its treatment is extremely expensive and therefore it is generally disposed of in a landfill. Another part of the salt already used is diluted in water, greatly complicating the subsequent purification processes of the residual floats. In fact, it is considered that more than 40% total dissolved solids (TDS) and 55% of chlorides in the resulting effluent of the total tanning process come from salt preservation.[7]

It is important to note that currently, in many cases, the hides are tanned a few days after the slaughter of the animal, which implies that very often a short-term preservation of approximately one month is enough. Another existing option is long-term preservation (salted or dried), which is absolutely required when the raw stock must remain stored for a long time before the start of the tanning operations.

For many years, a large number of researchers have tried to develop other preservation methods based on the total or partial replacement of salt by chemical products. In this regard research has been conducted on the hide preservation properties of chemicals such as boric acid combined with biocide[8] or naphthalene,[9] acetic acid combined with sodium sulfite[10] or with benzoic acid,[11] benzalkonium chloride,[12] formaldehyde,[13] sodium thiosulfate,[14] sodium metabisulfite,[15] sodium sulfate,[16] potassium chloride,[17] sodium carbonate,[18] oxide magnesium,[19] silicate,[20] silica-gel,[21] ozone,[22] synthetic polymers,[23] polysaccharides,[24] sodium hexafluorosilicate,[25] formic acid or formic acid combined with sulfuric acid,[26] chlorites and hypochlorites,[27] quaternary ammonium salts,[28] polyethylene glycol,[29] biocide,[30] and various antibiotics.[31-32]

Other lines of research include subjecting the hides to vacuum sealing,[33] cooling,[34] freezing,[35] electrical currents,[36] gamma irradiation,[37] irradiation with electron beams,[38] as well as the same irradiation combined with the use of bactericides[39] or with the use of gamma rays.[40]

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In recent years, several researchers have attempted to replace salt with plant-based formulations, thus valorizing the bioresources. Some of the plants tested were *Myrtus communis,*[41] *Origanum minutiflorum,*[42] *Azadirachta indica,*[43] *Sesuvium portulacastrum,*[44] *Wedelia chininsis*, *Cassia alata*, *Clerodendrum phlomidis*, *Solanum trilobatum* and *Calotropis procera,*[45] *Acalypha indica,*[46] *Terminalia chebula,*[47] *Lawsonia inermis,*[48] *Semecarpus anacardium,*[49] *Citrus sinensis,*[50] *Tamarindus indica,*[51] *Rumex abyssinicus,*[52] *Moringa oleifera*, *Averrhoa bilimbi*, *Muntingia calabura,* and *Leucaena leucocephala,*[53] The preservative action of these products is due to the fact that they contain antibacterial compounds.

The study presented in the paper follows this line of research studying the possibility of using wheat bran to replace part of the salt used in the short-time preservation of hides, thus contributing to improvements in the sustainability of the tanning process.

Wheat bran is one of three layers of the wheat kernel, specifically, the most external one. It is stripped away during the milling process and produces a very abundant and relatively inexpensive byproduct. It is estimated that 12 million tons protein from wheat bran are wasted annually worldwide.[54] Different alternatives to recycle such solid waste are being studied.[55,56] Wheat bran contains antibacterial and antioxidant compounds.[57] The most abundant one is ferulic acid,[58] but it also contains other phenolic acids (such as vanillic acid, syringic acid, coumaric acid), lignans[59] and alkylresorcinol.[60] For this reason, its potential use as a skin preservative has been studied.

Experimental

Materials

Bovine hide, wheat brand, and salt (NaCl) were used to carry out the tests.

Other equipment included a laboratory drum with temperature sensor (Inoxvic brand), a laboratory stove (Nahita brand), a laboratory scale (Cobos brand), and a pH meter (Crison brand).

Besides, p-iodonitrotetrazolium violet indicator (98%) was used to carry out the tests to determine hide putrefaction.

Methodology

The research was structured in five stages. The research is summarized in Table I and each stage is explained in detail below.

Test 1. Potential of wheat bran as a preservative of hides

The first stage consisted of a series of pre-tests to determine whether wheat bran may actually work as a hide-preserving agent.

In three of the tests wheat bran (25% on the weight of the hide) was applied solidly covering a piece of hide on both sides. In two of the tests 10% and 20% (on the weight of the hide) of salt (NaCl) were mixed with the wheat bran. The hides were then left to rest wrapped with a plastic at room temperature (approximately 20°C) for one month. Two clear symptoms of poor hide preservation are that the hair is easily pulled out and/or the smell of ammonia is detected. Each day the hides were unwrapped and these two tests were performed. Then the hides were wrapped again.

In another test, an amount of 40 g of wheat bran was mixed in 360 g of water and the amount of salt needed to reach a final density of 7.5°Bé (27.2 g). The mixture was stirred vigorously. The hide (40 g) to be preserved was introduced in the same container and allowed to marinate. When the float completely penetrated the hide reaching its center, the hide was removed from the float, wrapped in plastic and left to rest for a month at room temperature. The test was repeated carrying out the maceration at 40°C.

This last test was repeated changing the conditions of maceration. In this case the mixture of wheat bran, water and salt was allowed to stand in an oven at 40°C for three days before introducing the hide into the maceration vessel. The objective was to previously hydrolyze the bran so that the hide was macerated in an acidic solution at room temperature.

Table I

Summary of tests performed during the research

Test number	Test objective
1	Test to determine the potential preservative effect of wheat bran applied in different ways on the hide
2	Test to determine the preservative effect on the hide of wheat bran applied in liquid with different saline concentrations
3	Test to determine the preservative effect on the hide of wheat bran applied in liquid depending on the saline concentration and the maceration time
4	Test to compare qualitatively the presence of bacteria on the hide depending on the preservation method applied
5	Test to compare the physical properties between a hide preserved with salt and the hides preserved with the new methods tested with wheat bran

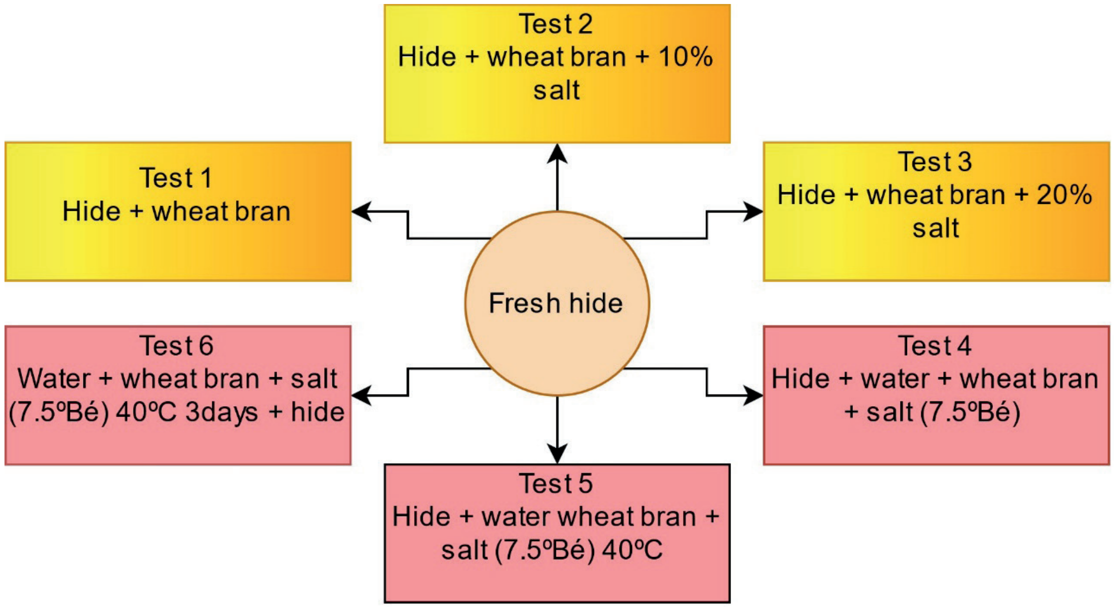

Figure 1. Tests on the hide preservative ability of wheat bran.

In these three tests the same controls were carried out as in the three previous tests. Figure 1 shows a diagram of the six tests carried out.

Test 2. Influence of the saline concentration in the preservation of hides

In the second stage the influence of the amount of salt on the preservation of a hide by maceration was studied by means of an aqueous mixture of wheat bran. Four identical solutions were prepared by mixing 40 g of wheat bran with 360 g of water. Increasing amounts of salt (41.5 g, 7.8 g, 100.8 g and 145.6 g) were added to each solution until saturation was reached. The final densities of each solution were 10, 15, 20 and 23.7°Bé. A piece of 40 g hide was immersed in each container and allowed to marinate. When the float completely penetrated the hide, reaching its center, the hide was removed from the float, wrapped in plastic and left to rest for a month at room temperature. The reference was an identical hide piece kept at 20°C without any preservation. Hair removal by pulling off, pH and the smell controls of the hides were performed periodically.

Test 3. Influence of maceration temperature and the moment in which the salt is added on the preservation of the hides

The third stage of the study examines how an increase in temperature during the maceration of wheat bran in water (with and without salt) may affect the preservation of the hide. Figure 2 shows a diagram of the eight tests carried out.

Two different types of maceration were performed. Eight identical solutions were prepared by mixing 40 g of wheat bran with 360 g of water. In four of the solutions, enough salt was added so that their final densities were 10, 15, 20 and 23.7°Bé. The maceration was carried out at 40°C until achieving pH stabilization. The solutions were allowed to cool to room temperature, filtered and then a piece of 40 g of hide was introduced in each of the containers. In the other four solutions a similar procedure was followed, although with a significant modification; the salt was added after maceration in the oven and just before introducing the hides into the already filtered solutions. Therefore, in some tests the maceration of the wheat bran, and therefore its acid hydrolysis, was carried out in saline medium and in the other tests the salt was added afterwards. When the float completely penetrated the hide, reaching its center, the hide was removed from the float, wrapped in plastic and left to rest for a month at room temperature. Hair removal by pulling off, pH and organoleptic controls of the hides were performed periodically.

Test 4. Comparison of the effectiveness of the preservation methods being tested

A comparative assessment of the degree of putrefaction of several of the hides preserved with wheat bran was carried out. The dry preservation method and the methods in which the preservation was carried out in liquid medium and had shown positive results were evaluated. In this

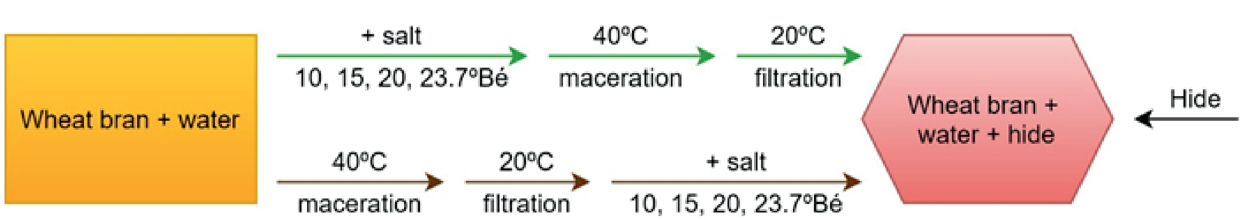

Figure 2. Different systems for preparing the preservative solution.

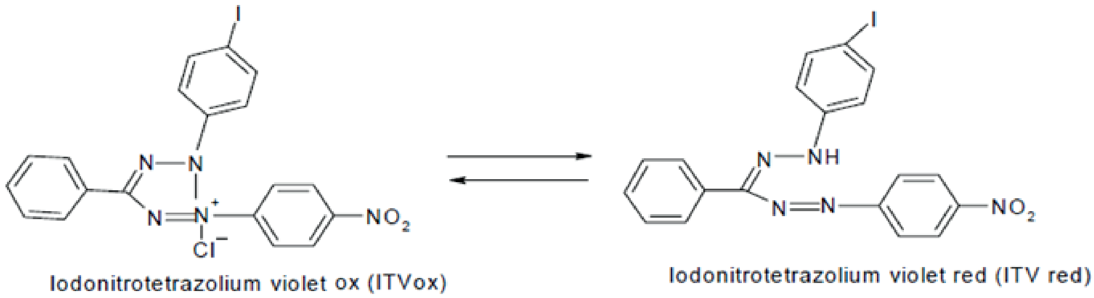

Figure 3. p-Iodonitrotetrazolium Violet reaction.

last case, only the three tests with minimal presence of salt (10 °Bé) were evaluated. The degree of putrefaction of the hide was measured using the p-iodonitrotetrazolium violet indicator. In the presence of bacteria, this indicator is reduced, forming a compound derived from formazan, which is violet colored and insoluble in water (Figure 3). This reaction can assess the degree of putrefaction of a hide.

Development of a comparative pattern to assess bacterial growth

In order to visually compare the effectiveness of each of the preservations a pattern was developed. A piece of salty hide was soaked for two days at room temperature so that bacterial growth would occur. Five test tubes were filled with different amounts of the resulting residual float, deionized water and p-iodonitrotetrazolium violet indicator, as shown in Table II.

The test tubes were left in an oven at 35 °C for 24 hours. Each tube modified its color depending on the number of bacteria it contained.

Comparison of bacterial growth in the various preservation methods tested

Six pieces of hide were subjected to the following preservation methods explained in the previous sections:

a) Wheat bran (dry).
b) 10% salt + wheat bran (dry).
c) 20% salt + wheat bran (dry).
d) Aqueous solution of macerated wheat bran + salt (10°Bé) at room temperature + hide.
e) Aqueous solution of macerated wheat bran + salt (10°Bé) at 40°C (3 days) + hide.
f) Aqueous solution of macerated wheat bran at 40°C (3 days) + hide + salt (10°Bé).

Table II

Comparative pattern. Content of each tube

Test tube	0	1	2	3	4	5
Indicator	1 mL	1 mL	1 mL	1 mL	1 mL	1 mL
Deionized water	5 mL	4 mL	3 mL	2 mL	1 mL	0 mL
Residual float	0 mL	1 mL	2 mL	3 mL	4 mL	5 mL

In the case of methods d, e and f, the tests were carried out with the minimum amount of salt (10°Bé) that had allowed obtaining good preservation results in previous tests.

The pieces were left in an oven at 35°C for 48 hours to accelerate possible bacterial growth. Subsequently they were soaked for two days at room temperature. Results showed that the final pH was the same for all floats. In six test tubes, 5 mL of each residual float was mixed with 1 mL of p-iodonitrotetrazolium violet indicator and left for 12 hours in an oven at 35°C. Finally, the coloration of each tube was compared with that of the tubes of the standard to establish a relative order of effectiveness of the preservation systems being tested.

Effect of salt on bacterial growth

An additional test was carried out to assess the preservation effect of the salt added to the aqueous solution of macerated wheat bran kept at 40°C for three days before adding the salt and the hide to be preserved. The process was similar to the one followed in the previous test except for the modification of doubling the amount of indicator to intensify the resulting color and thus facilitate the interpretation of the results. Five tests were carried out with densities of 0, 10, 15, 20 and 23.7 °Bé and the results were visually evaluated.

Test 5. Effect of the type of preservation on the physical properties of the final leather

Four pieces of hide were preserved for one month according to the following methods:

Wheat bran (dry).

Aqueous solution of macerated wheat bran at 40°C (3 days) + hide + salt (10°Bé).

Aqueous solution of macerated wheat bran + salt (10°Bé) at 40°C (3 days) + hide.

Salting (traditional).

In other words, from each of the different methods tested throughout the research, those with the highest salt savings that allowed to preserve the hide correctly were chosen.

The pieces of hide were chrome tanned following a standard formulation.

The Official IUP (Physical Test Methods) and IUC (Chemical Test Methods) methods specified below were followed to analyze the leather: *IUP 6 (ISO 3376:2011) Determination of tensile strength and percentage extension;*[61] *IUP 8 (ISO 3377-2:2002) Determination of tear load - Part 2: Double edge tear;*[62] *IUP 9 (ISO 3379:2015) Determination of distension and strength of surface (Ball burst method);*[63] *IUP 16 (ISO 3380:2015) Determination of shrinkage temperature up to 100°C.*[64]

Three experts compared the following organoleptic properties of the leathers obtained: fullness, softness, grain tightness, and grain smoothness.

Results and discussion

Test 1. Potential of wheat bran as a hide preservation agent
In the three tests in which the wheat bran was applied in solid form, the hides suffered significant dehydration. The test in which no salt was added after two days was practically dry (water content decreased from 70% to 15%) and maintained a constant pH of 6. When salt was added to the tests, less dehydration occurred, keeping the hides somewhat moist, and the pH value decreased slightly until 5.5. After one month none of the three tests showed any sign of putrefaction.

In the three tests in which the hide was macerated in aqueous solution, it took five days for the liquid to penetrate the hide. In the test carried out at room temperature, the pH dropped to 5. In the two tests with working conditions at 40°C, the final pH was 4.5. In all three cases, the hairs could be easily removed by pulling them off by hand after a few days since the beginning the test and the pieces of hide gave off a slight ammonia smell. That is, clear signs of putrefaction were observed.

In the first case, the preservative effect was due to dehydration, since bacterial growth was halted in the absence of water.

In the second case it was observed that the presence of salt was not enough to stop bacterial growth. It was also concluded that higher temperatures accelerate the acid hydrolysis of wheat bran, yet the compounds released were not capable of slowing bacterial growth on their own. Therefore, under the tested conditions, the preservation of the hides was not possible.

In summary, under the conditions tested, preservation of the hide with solid wheat bran is possible and preservation with wheat bran macerated in water is not possible.

Test 2. Influence of saline concentration on the preservation of hides
In the four tests the macerating solution crossed the hides in five days whereas the pH value remained between 5.5 and 6.

The blank test hide (no preservation) showed signs of putrefaction after 5 days. The hairs were easily removed by hand and the piece of hide gave off ammonia smell.

The four tests in which the maceration solution contained different amounts of salt (10, 15, 20 and 23.7°Bé) did not show differences in behavior. After one month none of the four tests showed any sign of putrefaction and the hairs were difficult to remove by simply pulling them off by hand. The hides were flexible, which means that they retained a significant degree of moisture.

Taking also into account the result of the previous test, in which the same procedure was followed although with a different amount of salt (7.5°Bé), it was concluded that the presence of a certain amount of salt (10°Bé) is necessary for the preservation method to succeed. The salt greatly contributes to stop bacterial growth and enables the preservation of the hides with no signs of putrefaction for at least one month.

Test 3. Influence of maceration temperature and the moment in which the salt is added on the preservation of the hides
After two days in the oven at 40°C, the pH of the macerating solutions without salt was 4.5 and this value remained constant. On the other hand, in the macerated solutions with salt the final stabilized pH was 5. This value was reached after three days in the oven at 40°C, except in the most concentrated saline solution when it was achieved in 4 days. In both cases, when the pieces of hide were introduced in filtered maceration solutions at room temperature, it took four days for the macerating solution to penetrate the hides.

After one month none of the tests showed any sign of putrefaction and the hair was extremely difficult to pull off by hand.

The results of the test show that the higher the temperature, the faster the hydrolysis of wheat bran, thus facilitating the appearance of acidic compounds that possibly influence the preservation of hides. The presence of salt slows acid hydrolysis and prevents the release of some acidic compounds, as indicated by the final pH difference between the two types of maceration solutions.

Test 4. Comparison of the effectiveness of the preservation methods

Development of a comparative pattern of bacterial growth
The colorations of the tubes that served as a comparative pattern can be seen in Figure 4.

The liquid contained in tube 0, which does not contain residual float from the soaking of hides, is transparent, and the coloration becomes violet as the amount of the residual float increases. Therefore, the

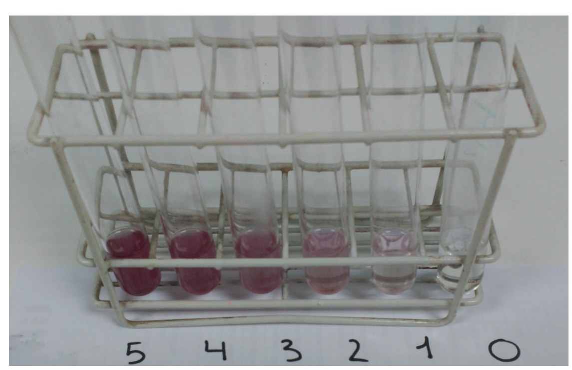

Figure 4. Comparative pattern of bacterial growth. More color intensity means more bacteria.

more intense the violet color in the tube, the more bacteria will be contained in the liquid.

Comparison of the bacterial growth in the different preservation methods being tested

In the comparative test, the final pH of all the residual soaking floats was 6. The colorations obtained at the end of the test can be observed in Figure 5 (tests a, b and c) and Figure 6 (tests d, e and f). The comparison with the pattern tubes may be found in Table III.

Results indicate that bacterial growth is more pronounced in the case of hides preserved by applying dry wheat bran. The addition of salt stops bacterial growth, but the other preservation systems tested slow it down to a much greater degree.

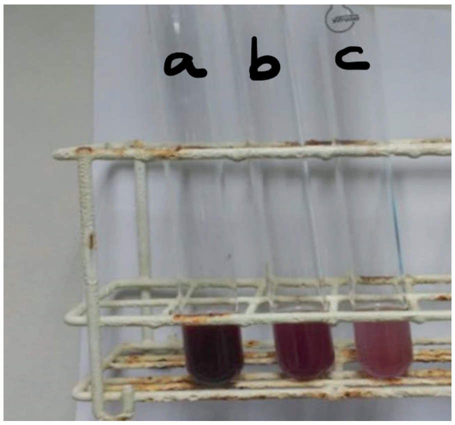

Figure 5. Bacterial growth versus dry preservation methods: **a.** Wheat bran; **b.** Wheat bran + 10% salt; **c.** Wheat bran + 20% salt.

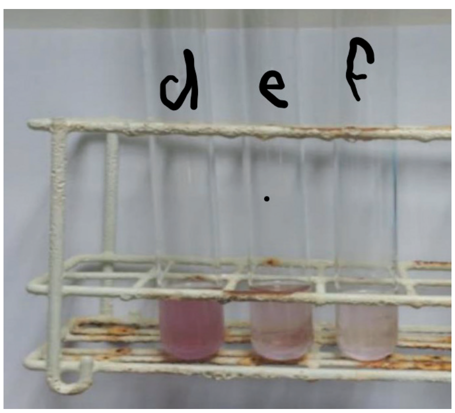

Figure 6. Bacterial growth versus aqueous solution preservation: **a.** Wheat bran + salt (10°Bé) at room temperature + hide; **b.** Wheat bran + salt (10°Bé) at 40°C + hide; **c.** Wheat bran at 40°C + hide + salt (10°Bé).

The reason is that in the absence of salt, bacterial growth does not stop until the piece of hide is dry. On the other hand, when the piece of hide is introduced into a saline solution, as the dissolved salt penetrates it, bacterial growth slows down. The penetration of the saline solution is faster than the drying, and as a consequence the bacterial growth stops sooner. However, as seen in previous tests, bacterial growth on preservation by drying stops quickly enough to allow the hide to remain in good condition for a month.

It is also observed that the heat treatment of the macerated aqueous wheat bran contributes to slowing down the bacterial growth in the hide. This is probably because the acid hydrolysis of wheat bran is encouraged by releasing compounds with a bactericidal effect. When performing the heat treatment without salt, the hydrolysis is even more salient, the final pH is lower and the bactericidal effect is clearly increased. The results suggest the need to carry out future investigations with longer preservation periods to check whether the effectiveness of the methods being tested is only short term or whether its effectiveness may persist in medium or long-term periods.

Effect of salt in bacterial growth

This test was carried out to assess the influence of the salt adding procedure for the hide preservation methods described in the previous test with lower bacterial growth.

The colorations obtained can be seen in Figure 7.

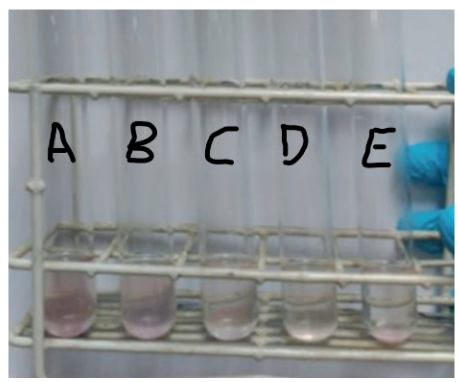

Figure 7. Effect of salt on bacterial growth. **A:** 0°Bé; **B:** 10°Bé; **C:** 15°Bé; **D:** 20°Bé and **E:** 23.7°Bé.

Table III

Comparison of the bacterial growth using the pattern tubes

Test	Coloring versus pattern tubes
Wheat bran (dry)	Much more intense than tube 5
10% salt + wheat bran (dry)	More intense than tube 5
20% salt + wheat bran (dry)	Similar to tube 5
Aqueous maceration of wheat bran + salt (10°Bé) at room temperature + hide	Between tube 3 and tube 4
Aqueous maceration of wheat bran + salt (10°Bé) at 40°C (3 days) + hide	Similar to tube 2
Aqueous maceration of wheat bran at 40°C (3 days) + hide + salt (10°Bé)	Similar to tube 1

Table IV

Results of physical tests

Type of preservation	Shrinkage Temperature (°C)	Tensile strength (N/mm2)	Extension (%)	Tear load (N/mm)	Distension (mm)
Salted (Traditional)	107.5	24.12	44.6	126.65	17.34
Wheat bran (dry)	106.5	29.91	31.1	109.09	17.80
Aqueous maceration of wheat bran at 40°C (3 days) + hide + salt (10°Bé)	108	23.32	40.5	103.26	16.28
Aqueous maceration of wheat bran + salt (10°Bé) at 40°C (3 days) + hide	107	29.68	49.0	162.70	16.17

It must be noted that in order to get a final color similar to that of the standard tube 0 (Figure 4, blank with no contamination) a density of 15°Bé in the preservation float was required. Likewise, it was observed that the higher the solution density, the lower the bacterial growth. Therefore, the results suggest that a solution with a density of 10°Bé enables a good preservation of the hide, at least in the short term.

Test 5. Effect of the type of preservation on the physical properties of the final chromium-tanned leather

The results can be seen in Table IV.

The differences in the results obtained are not significant and can be attributed to the own anisotropy of the hides. Therefore, from the viewpoint of physical properties, the four methods tested for the preservation of hides are equally acceptable.

All leathers showed good organoleptic properties except for the leather resulting from hides preserved in the aqueous maceration at 40°C. These showed some signs of grain cracking, which is indeed a serious inconvenience and therefore made us dismiss this method.

Environmental benefits

All the methods tested show significant savings in salt. Also, in most of the methods essayed wheat bran can be recovered for other uses by following the appropriate treatment. The majority of these uses are related to food, biochemistry or their use as fuel.

There are two salt preservation methods. The first one is with salt grain, in which case, at least 45-50% salt is used on the hide weight (Wu, 2017). Depending on the type of hide, this amount can reach up to 70-100%. In the second method, hides are tumbled in a paddle with saturated brine (36% w/v at 15°C), which is equivalent to a density of 26°Bé approximately, with a ratio kg hide/L float of 1/5 (Covington, 2011).

These methods are long-term preservation (2-3 years). Thus, in the three methods of dry application that were tested, salt savings range from 25% to 45% on the hide weight, when compared with the minimum quantities used in traditional salting.

In the two methods in which the wheat bran is macerated, the final solution contains 10.5% salt, while in a traditional preservation with brine it contains approximately 26% salt. These values are approximate since they vary slightly depending on the temperature. In any case, results show savings of 15.5% of salt per liter of brine. In both cases, the salt used is minimized by 50%. Whatever the chosen method, and taking into account that it is estimated that the annual salt expense to preserve skins is about 3 million tons, the proposed alternatives involve very significant savings in salt and, therefore, remarkable environmental benefits.

On the other hand, wheat bran can be recovered and reused. In the case of dry application, once the hide is preserved, the wheat bran can be recovered by shaking the hide. The washed and dried wheat bran can be reused (i.e. as a biofuel). In the case of application in a liquid medium, once the hide is preserved, the wheat bran can be recovered and reused after filtration, washing and subsequent drying.

Conclusions

Results show that the use of wheat bran in the preservation of hides avoids damage by bacterial attacks for at least one month. The systems successfully tested enable the hides to be preserved either by sprinkling the wheat bran on the hides or by macerating the wheat bran in water and subsequently impregnating the hides with the resulting solution. The quality of the final leathers obtained from hides preserved by the tested systems is comparable to the quality of leathers obtained from hides preserved by traditional methods. These new methods allow a very important reduction from the salt used in the traditional methods of hide preservation by salting, which leads to much better environmental outcomes, as has been explained above. The systems we have tested have proven to be valid for short-term preservation. Future research will be necessary to confirm or rule out whether the new systems are valid in medium or long-term periods.

Acknowledgements

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Extract of *Trema Orientalis (L.)* Stem Bark: A Potential Source of Environmentally Friendly Tanning Agent for Leather Industry

by

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Abstract

Researchers around the world are in continuous endeavor to develop environment friendly tanning agent due to adverse effect of conventionally used chromium during leather tanning. Recent trend of tanning is thus heading to chrome-free and greener chemical processing options. Vegetable tanning is an exoteric leather processing technique because of their lower pollution load on the environment. Considering the inadequacy and high costing for the commercialized tannins, development of alternative tannins from locally available plants and their characterizations are important. In this research, the stem barks of *Trema Orientalis (L.)* were extracted at different temperatures employing water solvent with or without additives (sodium hydroxide or sodium sulphite) to attain phenolic-rich extractives. To ascertain appropriateness as a vegetable tanning agent, the obtained extracts were thereafter characterized in respect to yield, total phenolic content, tannin content and molecular structure. The extraction yield for all extracts improves and the quality remains nearly unchanged with temperature rising. The elevated concentration of chemical additives enhances the extraction yield but lessens the quality of extracts. In terms of extraction yield and the quality of extracts the best condition for extraction was discerned at 80°C with water solvent. This water extract has a decent extent of phenolic and tannin content of 266.13 mg Gallic acid equivalent/ gm of dry extract and 30.12% respectively. The final extract exhibits excellent leather retanning tendency comparable to the commercial *quebracho* tannins.

Introduction

In leather industry, tanning is the chemical process where the putrescible animal hides and skins are converted to leather.[1] Through tanning process the raw hides or skins are converted to a durable material and ready for wide range of end applications.[2] During tanning, tanning agents directly link to the leather through the functional group of collagen and exhibit physical & chemical resistance.[3] The common tanning techniques are mineral tanning, chrome tanning, aluminum tanning, aldehyde tanning, vegetable tanning, oil tanning, combination tanning, etc.[4] Different characteristics are obtained from different tanning methods.[5] Amongst these, chrome tanning is globally most popular technique for leather tanning where chromium (III) salts are employed.[6] About 85% of all leathers produced globally are according to the chromium tanning method.[7] Chrome tanning, a 100 years old tanning technique, is one of the greatest inventions in the history of leather making.[8] Although chrome tanning has been proven as an excellent tanning technology; lack of proper handling might lead to possible risk associated in term of toxicity relating to hexavalent chromium.[9] It is crucial to assure 100% safety for people connected in leather production, for the environment and for the leather product end user in order to be compliant with today's sustainability standards. Vegetable tanning techniques are current trends in tanning for sustainability of the leather industry.[10]

Vegetable tanning processes are performed employing natural vegetable tannins which are available in powder or liquid form and are obtained from leaves, bark, roots, fruits, seeds or galls of plants.[11,12] Tannins are polyphenolic compounds with molecular weight ranges of 500 to 20,000 Da, soluble in water and capable of forming reversible and irreversible complexes with proteins, polysaccharides, alkaloids, nucleic acid & minerals.[13] The greater affinity of tannins for proteins is assigned by the number of phenolic groups in tannins since at the peptide bond in protein this is the binding position to carboxyl carbon.[14] Based on to the chemical structure tannins are classified into hydrolysable and condensed tannins.[15] Hydrolysable tannins carry a polyhydric alcohol in center, for example glucose and hydroxyl groups which is partially or fully esterified with gallic acid (gallotannins) or hexahydroxydiphenic acid (ellagitannins).[16] Condensed tannins are oligomers or the non-branched polymers of flavonoid units.[11,17] In leather tanning, the interaction mechanism between vegetable tannins and collagen of skin differs depending on such classes of tannins because of their distinct structures.[18] Both hydrolysable and condensed tannins are capable of forming powerful complexes with certain types of protein though they are structurally different. Condensed tannins are more preferred than hydrolysable tannins but their combination produces excellent leathers.[13]

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Most of the plant species in the world provide tannins but only a few of them contain acceptable extents necessary for commercial interest of leather tanning.[6] Mimosa, quebracho, chestnut extracts etc. are commercial tannins used for leather tanning and retanning technology.[3] Because of the insufficiency and high price involved for the commercially available tannins; the use of these tannins is limited for the cottage tanners.[19] So, the development of alternative tannins from indigenous plants and their characterization is crucial.

T. Orientalis (L.), locally known as Nalita, is a shrub and rapid growing tree belonging to the Family of Ulmaceae.[20,21] It is widespread in Bangladesh as well as many other countries like India, China, Nepal, Myanmar, Japan, Philippines, Indonesia, Malaysia, Saudi Arabia, Ghana, Senegal, Cote d'Ivoire, Australia, Brunei, Kenya, Sudan, Tanzania, Uganda, Vietnam, Zimbabwe etc.[21,22] It is widely used for medicinal purposes such as remedy of coughs, sore throats, asthma, bronchitis, gonorrhea, yellow fever, toothache and dysentery.[23] In addition to that it is also used in paper making.[24] Literature shows that *T. Orientalis (L.)* plant consists of rich amount of phenolic compounds.[21,25–28] Despite containing satisfactory amount of phenolic compounds still no research has been executed for selecting the appropriateness of *T. Orientalis (L.)* as vegetable tannin source for applying in leather industry. The objective of the present work was to assess the prospect of *T. Orientalis (L.)* stem bark's extract as an alternative to conventional vegetable tanning or retanning agents.

Experimental

Materials

T. Orientalis (L.) stem bark was collected from the garden of Pulp and Paper Research Division, BCSIR Laboratories Dhaka, Bangladesh Council of Scientific and Industrial Research. Then it was air dried and milled to powder using an analytical grinder. Hide powder was obtained from Chemical Research Division. The gallic acid was certified reference material (CRM) grade and other chemicals were analytical grade. The chromed tanned leather was obtained from leather processing division.

Extraction Process and yield of extract Calculation

For each extraction process 20 gm powdered bark was immersed in a glass beaker containing 400 ml distilled water which was then placed in a water bath. The beaker was covered with aluminum foil to prevent water evaporation. The processes were conducted at 50° and 80°C except stirring for 4 h either by water only or subsequently adding sodium hydroxide (0.5 and 1.0% of dry bark weight) or sodium sulphite (2.0% of dry bark weight). Then the extracts were filtered through vacuum filter and the filtrates were concentrated by a rotary evaporator at 60°C and finally freeze dried.

The Yield of extract was calculated as:

Yield (%): (Weight of oven dried extracts in grams/ Weight of the oven dried *T. Orientalis (L.)* bark in grams) × 100

Total phenolic content determination

Total Phenolic Content were measured by the Folin-Ciocalteu method[29] according to the literature.[30] For calibration curve the gallic acid was used as standard and the results were expressed as the total phenolic content in milligram of gallic acid equivalent (GAE) per gram of dry extract.

Determination of tannin content

Tannin content was quantified by hide-powder method (SLC117) as stated in literature [13] and is described as the extent of soluble solids of tannin extract is being absorbed by standard hide powder. So, the tannin content (%) was calculated from the difference between the total soluble solids (%) and the soluble non tannins (%).

Identification of tannin class by FT-IR spectroscopic method

The molecular structure of extracts/tannin was studied by Perkin Elmer FT-IR Spectrophotometer (Frontier) equipped with an ATR unit at a resolution of 4 $cm^{-1}$with 32 scans in the frequency ranges of 4000–600 cm^{-1}.

Retanning process of leather

The retanning processes of conventionally processed wet blue goat skins (chromed tanned leather) were executed by applying *T. Orientalis* stem bark extract (extract obtained at 80°C with water solvent) as experimental trial and commercial *quebracho* tannin as control trial. In both trials 8% tannin (based on dried weight of wet-blue material) and 1% syntan were used.

Characteristics of retanned leather

The retanned leather of experimental and controlled trials were finally characterized in terms of tear strength, tensile strength and percent elongation at break according to the SATRA TM 162, TM 43 and TM 43 respectively.

Results and Discussion

Extraction yield

The extraction processes were conducted at 50° and 80°C temperature employing water with or without additives (NaOH or Na_2SO_3). Water was chosen as solvent in this study by reason of on industrial scale other solvents were regarded problematical especially with respect to pollution, recycling and cost.[31] Table I exhibits the results of extraction yield and other characteristics of *T. Orientalis (L.)* stem bark extracts at different extraction conditions along with the properties of commercially used tannin *quebracho*.

Table I

Extraction yield and characteristics of *T. Orientalis* stem bark extracts and *quebracho* tannin

Extracts/Tannins	Solvent	Additives	Temperature (°C)	Yield (%)	Total Phenolic Content (mg GAE*/dry extract)	Tannin Content (%)
Quebracho	Unknown	-	-	-	510	57.56
T. Orientalis (L.)	Water	-	50	7.24	264.45	30.12
	Water	-	80	12.14	266.13	30. 36
	Water	Na_2SO_3 (1 %)	50	8.21	257.41	15.78
	Water	Na_2SO_3 (1 %)	80	13.18	257.19	14.98
	Water	Na_2SO_3 (2 %)	50	11.34	258.56	13.25
	Water	Na_2SO_3 (2 %)	80	17.31	258.61	12.68
	Water	NaOH (0.5 %)	50	25.80	60.46	<5
	Water	NaOH (0.5 %)	80	37.39	49.09	<5
	Water	NaOH (1.0 %)	50	33.60	49.33	<5
	Water	NaOH (1.0 %)	80	46.30	32.41	<5

*GAE-Gallic Acid Equivalent

Depending on the extraction condition the extraction yield of *T. Orientalis (L.)* stem bark extracts were ranges from 7.24-46.30% (Table I). The highest yield (46.30%) was attained for extraction with water plus 1.0% NaOH at 80°C temperature. The extraction yield of all extracts were increased with temperature rising (Figure 1) due to the improvement of compound solubility at higher temperatures as well as may be because of the enhancement of mass transfer to the liquid from the matrix of bark.[3] The yield of extractions were remarkably enhanced with increment of alkalinity of NaOH (Figure 2) as a result of rising solubility of lignin in NaOH solution[32] and considerable quantity of lignin were previously identified in *T. Orientalis (L.)* plant.[20,24,33,34]

Characterization of extract

Though the yield of the extraction indicates the performance of extraction, the suitability of extracts for leather tanning or retanning process relies on its characteristics such as total phenolic content, tannin content, types of tannin, etc.

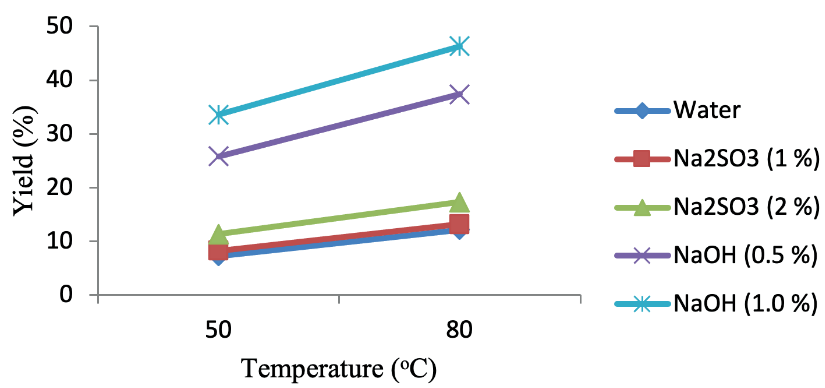

Figure 1. Effect of temperature on extraction yield of *T. Orientalis (L.)* stem bark extracts in water and alkaline solution.

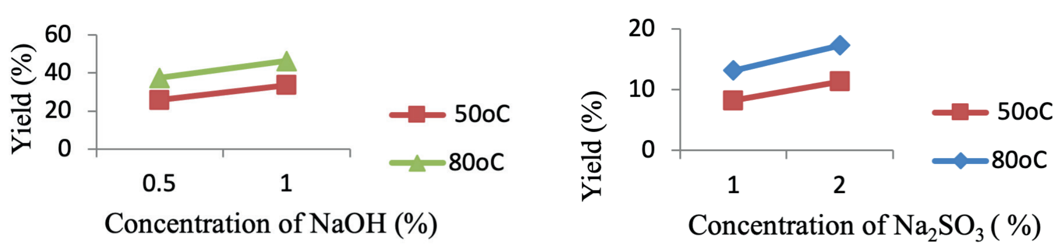

Figure 2. Effect of alkalinity on extraction yield of *T. Orientalis (L.)* stem bark extracts at different extraction temperature.

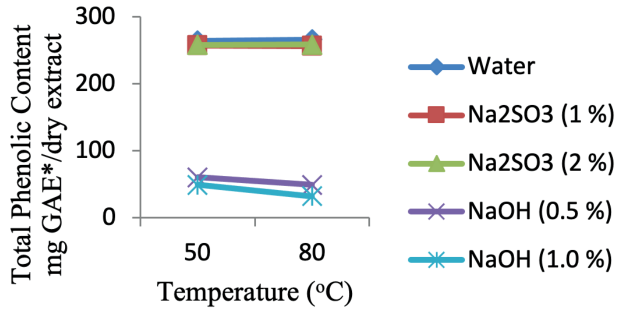

Figure 3. Effect of temperature on Total Phenolic Content of *T. Orientalis (L.)* stem bark extracts in water and different alkaline medium. *GAE-Gallic Acid Equivalent

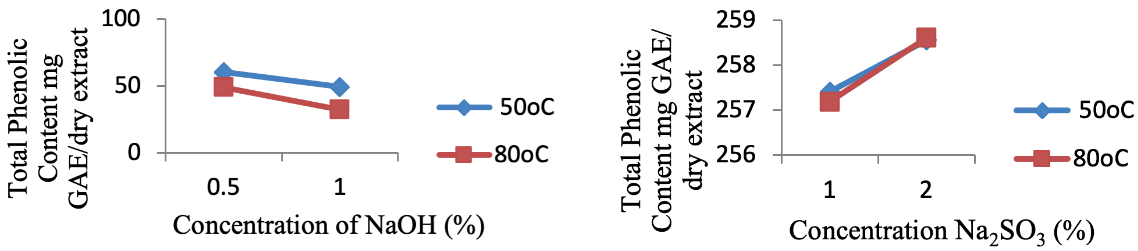

Figure 4. Effect of alkalinity on Total Phenolic Content of *T. Orientalis (L.)* stem bark extracts at different extraction temperature.

Total phenolic content and tannin content

Water extracts of *T. Orientalis (L.)* bark exhibits, for all extraction temperatures essayed, remarkably higher total phenolic content than alkaline extracts (exception for sulphited extracts). The influence of temperature on total phenolic content at different extraction medium was not significant (Figure 3). Greater alkalinity of NaOH reduced the phenolic contents remarkably (Figure 4), these happened since the alkali improved the solubility of non-phenolic compounds such as lignin in the course of extraction processes, as earlier discussed. The maximum value of total phenolic content (266.13 mg GAE/gm of dry extract) was found for the extraction with water at 80°C temperature and minimum value (32.41 mg GAE/gm of dry extract) was for the extraction with water plus 1.0 % alkali at 80°C temperature (Table I). A research performed in Ivory Coast showed that water extract of *T. Orientalis (L.)* bark had a total phenolic content of 240.73 mg GAE/gm of dry extract,[35] which is almost similar to the data found in our analysis.

Similar to the phenolic content of *T. Orientalis (L.)* bark extracts, extraction temperature did not show pronounced effect on tannin content (Figure 5). Higher alkalinity of Na_2SO_3 slightly reduced the amount of tannin content (Figure 6). The highest value of tannin content (30.36%) was observed for extraction with water at 80°C temperature (Table I) and the lowest value (not shown in table) was achieved for extraction with water plus 1.0% NaOH at 80°C.

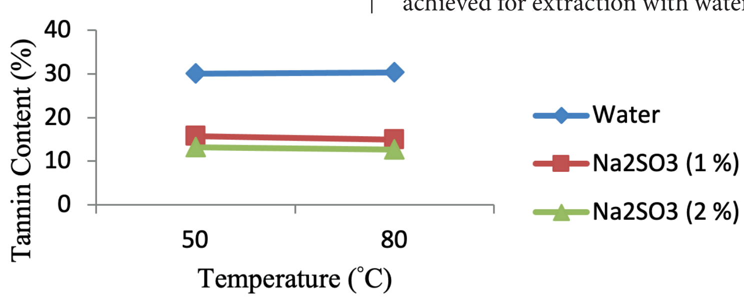

Figure 5. Effect of temperature on Tannin Content of water and sulphited extracts T. Orientalis (L.) stem bark.

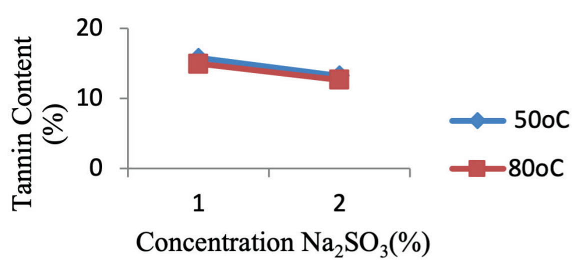

Figure 6. Effect of concentration of Na_2SO_3 on Tannin Content of extracts of *T. Orientalis (L.)* stem bark at different extraction temperatures.

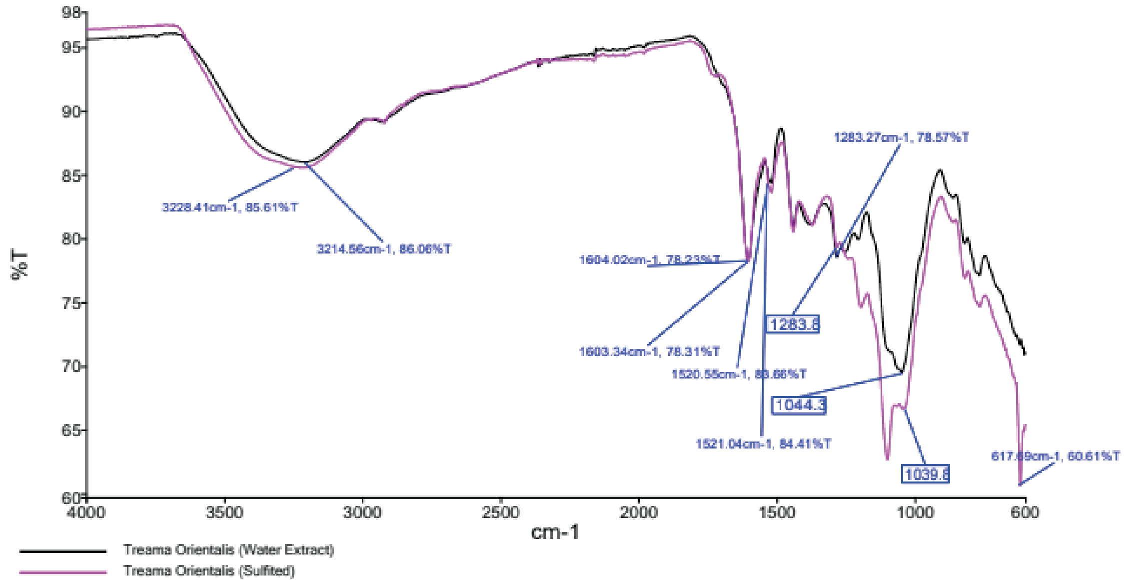

Figure 7. FT-IR spectra of water and sulphited extract of *T. Orientalis (L.)*

FT-IR Analysis

According to their molecular structure tannins are classified into hydrolysable and condensed tannins. In leather tanning condensed tannins are more preferred than hydrolysable tannins. FT-IR spectrum was used for identifying the molecular structure of water and sulphited extract of *T. Orientalis (L.)* stem bark (Figure 7). Commercial *Quebracho* tannin was used as control. NaOH extract was not considered in this analysis because of its lower tannin content.

Hydrolysable tannins exhibit spectrums band in the region of 1722–1702 cm^{-1} for the C=O stretching of esters, basically gallic acid derivatives.[36] These types of tannins also represent spectra at 1325–1317 and 872–870 cm^{-1} for symmetric stretching of C-O bond of ester and the presence of gallotannins (subclasses of hydrolysable tannins) respectively.[37] For *T. Orientalis (L.)* extracts and selected commercial tannins no peak was observed in these areas. Condensed tannins show medium to strong peaks of C=C–C stretching between the region of 1555–1503 cm^{-1}.[36] The spectrums of 1288-1283cm^{-1} are the indication of flavonoid-based condensed tannin, which is allocated to the ethereal C-O asymmetric stretching vibration from pyran-derived ring structure.[37] The sharp bands near 1520 cm^{-1} and 1283 cm^{-1} for both water and sulphited extracts indicates the existance of condensed tannin in *T. Orientalis (L.)*. The commercially known condensed tannin *Quebracho* also shows spectrum in these regions (spectrum not shown). The spectrum in the region of 680-600 cm^{-1} is attributed for the C-S vibration of sulfonic groups.[31] Reasonably, water extract does not expose any peak in this region and suphited extract represents this peak at 617 cm^{-1}. Though the extraction method is unknown, the absorption band in the 680-600 cm^{-1} area represents the possibility of sulfitation extraction method for *Quebracho* tannin.

Characterization of retanned leather

The properties of leathers retanned with *T. Orientalis (L.)* extract and commercial *Quebracho* tannin is given in Table II. The test results of tear strength, tensile strength and % elongation at break of leather retanned using *T. Orientalis (L.)* extract were comparable with leather retanned with commercial *Quebracho* tannin.

Table II

Characterization of retanned leather

Retanned leather	Tear strength (N/mm)	Tensile strength (N/mm^2)	Elongation at break (%)
Experimental trial	30.6±0.4	15.26±0.2	34.8±0.5
Controlled trial	31.15±0.3	15.60±0.4	36.2±0.7

± sign indicates the standard deviation of the measured values

Conclusions

The current work was done to utilize the stem bark extracts of the locally available *Trema Orientalis (L.)* plant as a leather retanning agent. The results of extraction yield, total phenolic content, tannin content and molecular structure of the all *T. Orientalis (L.)* stem bark extracts prove that extraction with water at 80°C provides the best quality extract. The final retanned leather exhibits excellent properties comparable with leather retanned by commercial *Quebracho* tannin. This research gives fruitful results for potential utilization of *T. Orientalis (L.)* plant as tannin source for increasing the supply of tannin towards improvement leather sector in Bangladesh and other countries.

Acknowledgement

Authors wish to convey thanks to Leather Research Institute, Bangladesh Council of Scientific and Industrial Research, Savar, Dhaka, Bangladesh for providing all facilities and funding.

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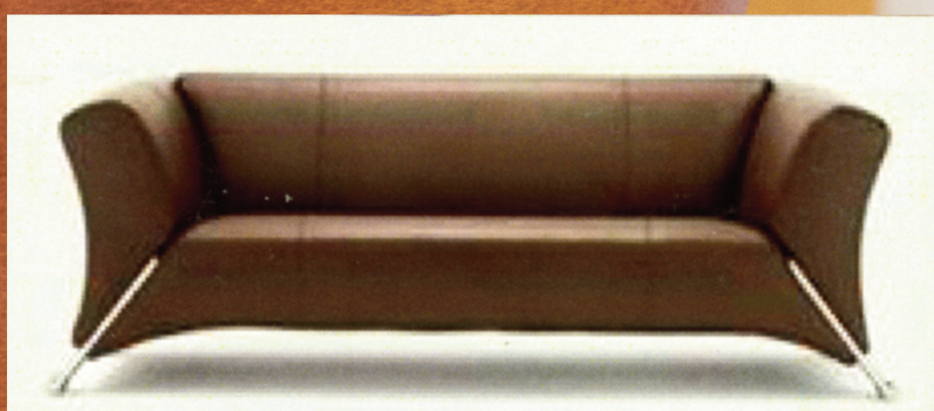

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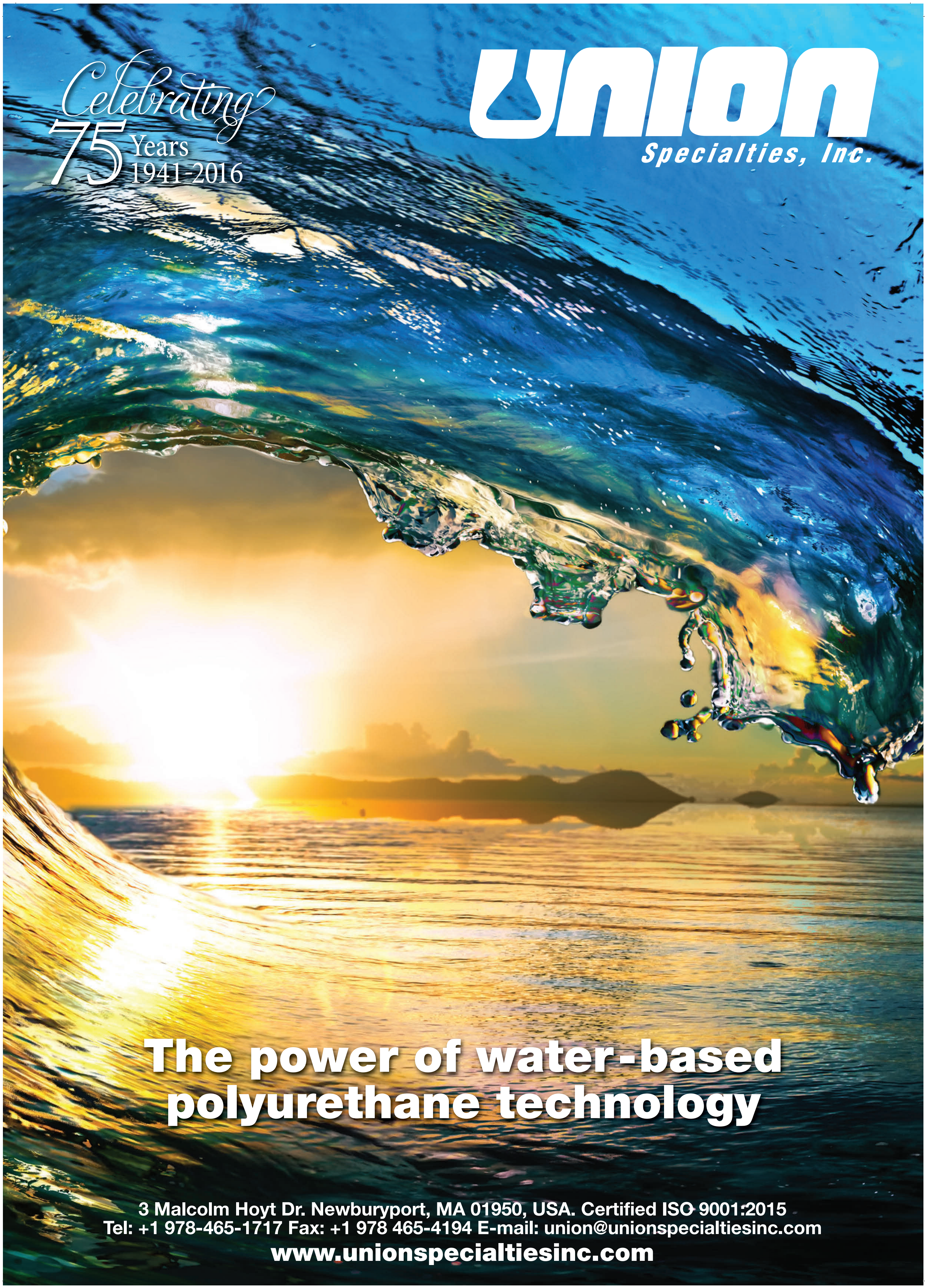
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COUNCIL CONFERENCE CALL MINUTES
AMERICAN LEATHER CHEMISTS ASSOCIATION
FALL COUNCIL MEETING

November 11, 2021

Present

Officers:	Mike Bley, Joe Hoefler
Council Members:	Shawn Brown, Jose Gallegos, Steve Lange, Lee Lehman, and John Rodden
Executive Secretary:	Carol Adcock

1. **WELCOME**. President Mike Bley called the meeting to order. He hoped everyone was doing okay and that the Convention would be able to be held next year. It was determined that a quorum was present.

2. **MINUTES.** All previous minutes have been approved by Council.

3. **2022 UPDATE OF ANNUAL CONVENTION.** Bill Clippinger, 2022 Convention Chair, was absent so Mrs. Adcock gave the following report regarding the 2022 Annual Convention preparations:

Contract Provisions

The 2022 site will be Eaglewood Resort & Spa, Itasca, IL, June 21-24. A deposit of $2,000 is on file with Eaglewood with another $1,500 being due 12/31/2021, another $2,000 due 5/17/2022 and a final deposit of $2,000 due 6/20/2022.

The rates will be as follows:

Single $415.54 per night, inclusive
Double $568.58 per night for two, inclusive

Rates quoted are per night and include lodging, breakfast, lunch, dinner, all taxes and amenity fee. Package begins with lunch on day of arrival and ending with breakfast on day of departure. He stated that the deadline for reservations is Friday, May 27, 2022.

The rates for pre/post arrival are as follows:

Single/Double $189 per room plus taxes and fees = $209.37
Rates for early arrival include accommodation only.

Schedule

The tentative schedule for the convention was previously emailed to Council. It is identical to the 2018 convention at Eaglewood. Mrs. Adcock will contact Buckman to see if they are interested in sending their golf analyzer as in previous years.

Mr. Lehman was asked to talk to Council about a proposal from Sarah Drayna concerning the LACA and its next meeting in Chicago. Discussion followed about combining their meeting with our annual convention. Council felt it needed more facts and details. Mr. Lehman will speak to Mrs. Drayna and Mr. Hoefler will talk to Steve Sothmann about this.

Entertainment

Bowling at Kegler's is scheduled on Wednesday evening, June 22. There is also darts and pool tables plus an open bar for most of the evening as well as food.

Sponsorship Campaign

Mrs. Adcock reported that the sponsorship campaign for 2022 will be the same as the one for 2019. Donis Bosworth as Convention Vice Chair will start the campaign in early 2022.

Sports and Social Coordinator

Mrs. Adcock reported that Mr. Clippinger does not need a Social Coordinator for 2022, but he will ask someone to be the Sports Coordinator for the golf tournament.

Proposed Budget

A proposed budget for the 2022 convention was emailed to Council for their review. It was reviewed during the call. Motion was made, seconded and unanimously passed to approve such budget as presented.

AV Person

Mr. Clippiner will find an AV Coordinator for 2022.

Technical Program – Joe Hoefler, Chair
Mr. Hoefler will start contacting those who agreed to give a paper in 2020 or 2021 and see if they are still willing to present. He reported that several of his past commitments have retired so the number of papers he has may be reduced. Council will help get confirmed presenters. Mr. Hoefler plans to complete the program no later than early March.

Wilson Lecture – David Peters, Chair
Randy Johnson with GST AutoLeather, Inc. will present the 2022 Wilson Lecture. He was informed of the date change and has agreed to giving it on June 22. Mrs. Adcock will contact him about a name change for his company and make sure he has the guidelines for the lecture.

Alsop Award – Joseph Hoefler, Chair
The 2022 recipient of the O'Flaherty Service Award was submitted to Council earlier and the recipient has been approved by Council.

O'Flaherty Service Award – Sarah Drayna, Chair
The 2022 recipient of the O'Flaherty Service Award was submitted to Council earlier and the recipient has been approved by Council.

2023 Convention Site
Mrs. Adcock reminded Council of Mr. Clippinger's previous suggestions about returning to Grandover Resort in Greensboro, NC for our next convention. He felt it might be easier to return to a previous convention site since he is new to this position. The convention was held at Grandover in 2003, 2008 and 2012. He also recommended the site due to its close location to the hotel and the fact that the hotel provided a shuttle from the airport to the hotel. Previously Council had suggested that Houston might be a possible site since Mr. Clippinger officed there. It was also felt that a Houston site might encourage people from Mexico to attend and would be easier for international participants. Council would like Mr. Clippinger to look into Grandover as well as sites in Houston and report back to Council in the next few months. Dates for the convention will be dependent on rates, but it was suggested that the end of the month was not a good date for the convention as people might be leaving on vacation by then. Room nights for the convention will be as usual, namely 25 for Monday night, 60 for Tuesday and Wednesday nights, and 50 for Thursday night.

4. **FINANCIAL REPORTS** – Carol Adcock
Year to Date Financial Reports
Council reviewed the Profit and Loss Statement and Balance Sheet through October 31, 2021.

The Membership Breakdown as well as a dues and subscriptions breakdown for 2022 was handed out and reflected the following:
119 Active, 44 Active Life, 4 Active Life Mutual, 20 Active Life Retired, 13 Active Mutual, 39 Active Retired, 1 Student, and 31 SLTC along with 2 SLTC Students, for a total of 273 members. Out of the above membership that is anticipated for 2022, dues will be collected from 125 paying members, excluding the dues that will be collected from the SLTC members. The list of canceled memberships was reviewed. There are 50 subscriptions that have been invoiced for renewal for 2022.

Mrs. Adcock also noted that 1 advertiser in the Journal for 2022 has agreed to advertise again in 2022 and has paid. She will be contacting the other 4 advertisers to see if they will also advertise in 2022. She also hopes to contact new companies about advertising.

Motion was made, seconded and passed to accept the Financial Reports as submitted.

A rough draft of the 2022 Association Budget was reviewed. Mrs. Adcock noted there was no need for the Lollar award as the next IULTCS Congress will not be until 2023. Discussion was held with a motion being made, seconded and carried to approve the 2022 proposed Association Budget after taking the Lollar Award off. The revised budget is attached to these minutes.

5. **EDITOR'S WRITTEN REPORT** – Steve Lange
November 10, 2021

Dear ALCA Officers and Councilors:
We are on track to publish 46 papers in 2021. Seven papers rejected have been rejected in 2021. The flow of papers has increased along with the diversity of the topics. Currently, have full issues assigned through April 2022, basically a six month window. This seems like too long of a buffer. My understanding of previous years is that the buffer ranged from 3 to 4 months. The Editorial Review board is working on 8 papers. Reviews for 9 papers have gone back to authors for revision. Twenty papers are pending publication. For 2020 and 2021 to date, the Top Ten Abstract and Article views are summarized on the next page.

Respectfully submitted,
Steven D. Lange, *Journal* Editor

Mr. Lange also submitted a JALCA Website Analysis from January 2020 to November 10, 2021. It reflected the top ten article abstracts viewed, with the top receiving 399 views. The chart also reflected the top ten whole article views, with the top one receiving 59 views.

Discussion followed regarding the number of papers being submitted for publication. Mr. Lange reported that it had been down so he only published three papers in the March and April issues. However, there has been an increase in papers and he has been able to do the usual 4 papers every since. He also reported that he has enough papers to do 5 per issue for a little while. It was felt that we should keep to the 4 papers per issue to see if the flow of papers continues.

Motion was made, seconded and unanimously passed to accept the Editor's Report as written.

6. **WAYS AND MEANS COMMITTEE REPORT** – Shawn Brown and Steve Schroeder
Mr. Brown submitted the following written report:

Here is some of the highlights and overall review of the plan:
Balance on January 1, 2021: $198,658.70
Withdrawals during 2021 (so far, through Nov 3, 2021): $47,978.
Current balance as of Nov 3, 2021: $191,709. 21
The overall gross return of the account (strictly performance), the account has been up +20.65% year to date.
Obviously, the withdrawals although necessary for the operations of the ALCA have consumed all the growth.

Current portfolio allocation is:
Approx. 19% - Home Depot stock - have a large gain on this position and current dividend yield is approx. 1.80%

Mutual funds allocation:
Approx. 23% is in Growth Fund of America (growth / equity oriented)
Approx. 29% is in American Balanced Fund (which is 50% growth / equity and 50% cash / money market / fixed income bonds)
Approx. 25% is in Washington Mutual Fund (which Is a blue chip, high dividend paying fund with a growth / equity / value-oriented blend)
Approx. 4% is in money market / cash account

Overall profit on the account overtime (despite the withdrawals) is:
Total invested: $107,158.57 and current value is $191,709.21

The portfolio managers are not suggesting any changes to the allocation of the portfolio at this time.

Best Regards,
Shawn Brown

Discussion followed regarding how well the portfolio was doing. Mrs. Adcock pointed out that it had made a significant gain between the end of September and the end of October.

Motion was made, seconded and unanimously passed to accept the Editor's Report as written.

7. **TECHNICAL COMMITTEE REPORT**
Since there is no current chair of the technical committee, no formal report was submitted. Mrs. Adcock reported that the Education Subcommittee was still overseeing the Leather Correspondence Course and the Methods and Specifications Subcommittee was still overseeing the Randall Rowles Memorial Scholarship. The Chair of the Education Committee had asked for his 2022 dues to be waived as he was unemployed. Motion was made, seconded and unanimously approved that his dues be waived for 2022 for his service to the Association.

It was agreed that Council will discuss the future of the Technical Committees at their next meeting during the convention in June.

8. **NOMINATING COMMITTEE REPORT –** David Peters, Chair
Mrs. Adcock had contacted Mr. Peters prior to the meeting. He has asked to be replaced as Chair of the Nominating Committee as he is now retired. The committee did have a Vice President Candidate and he is still willing to serve. There is still a need for four Councilor candidates. It was felt that a replacement needed to be found for Mr. Peters and that it should be a former President of the ALCA according to the guidelines for the committee. Council will be working on this.

9. **OLD BUSINESS**
Finances of the Association
The finances of the Association are doing pretty well since dues and subscriptions for 2022 are starting to be paid.

10. **NEW BUSINESS**
There was no new business to come before Council.

11. **LOCATION AND DATE OF NEXT COUNCIL MEETING**
It was felt that another conference call was needed in early February. A date will be circulated closer to that date.

There being no further business before Council, the meeting was adjourned.

Respectfully submitted,
Carol Adcock, Executive Secretary

THE AMERICAN LEATHER CHEMISTS ASSOCIATION
2022 BUDGET
Approved November 11, 2021

INCOME:		
Advertising	$16,812.00	
Copyright Income	500.00	
Correspondence Course	3,000.00	
Dues	30,275.00	
Postage & Handling	2,700.00	
Reprints/Articles	500.00	
Subscriptions	11,500.00	
Registration	22,750.00	
Sponsorships	32,000.00	
Dividend	3,000.00	
Total Income		**$123,037.00**
EXPENSES:		
Bank Wire fee	350.00	
Bank Service Charges	25.00	
Copyright	780.00	
Communication Expenses		
Website	1,000.00	
Fax	130.00	
Telephone	900.00	
Credit Card Processing Fees	3,000.00	
Discounts Given	1,900.00	
Dues & Subscriptions	480.00	
Insurance Expense		
Businessowners Coverage	450.00	
Employee Dishonesty	191.00	
Worker's Compensation	335.00	
License, Fees, and Permits	30.50	
Membership Development	20,000.00	
Office Expenses: Supplies	1,500.00	
Office Expenses: Postage	525.00	
Office Expenses: Printing & Postage	27,000.00	
Office Expenses: Rent	8,100.00	
Payroll Expenses		
Gross Wages	49,644.00	
FICA	3,077.93	
Medicare	719.84	
Professional Fees		
Accounting	1,200.00	
Editor	15,600.00	
Rowles Scholarship Fund	500.00	
Total Expenses		**$137,438.27**
NET INCOME/LOSS		**($ 14,401.27)**

Lifelines

Murali Sathish, see *JALCA* **110**(11), 379, 2015.

R. Aravindhan, see *JALCA* **106**, 208, 2011

J. Raghava Rao, see *JALCA* **93**, 156, 1998.

Fernando Lado has a Bachelor's degree in Chemistry, Universidad de la República, Uruguay in 1992 and further studies in Biochemistry in 2000. Since 1992 he has been working in the leather industry, starting in Curtiembre Branaa in Montevideo which later became Zenda Leather and finally as part of JBS group. Starting as leather technician in the Wet-End with several works and developments in this field, then he assumed Project Manager for the development of chrome-free leather in 1998 for automotive OEMs. Since 2009 to 2016 he was in charge for global operations for Zenda and up to present is responsible manager for finishing and cutting in Uruguay, Mexico and Europe.

Ricardo Tournier earned a degree in Chemical Engineering from Universidad de la República, Montevideo, Uruguay in 1968 and a MSc in Chemical Engineering from University of South Carolina, USA in 1971. In 1974 he attended a Dyestuff Course at the Chemistry Department of Turin University and a Practical Course on hide tanning at Instituto "Baldracco," Turin, Italy. Started in the leather industry in 1971 at Lanza Tannery, Uruguay, for 9 years. Later he worked for 20 years as Technical Manager at Paycueros Tannery, a member of SADESA Group. From 2000 to 2012 he was Technical Assistant to the General Manager at Zenda Leather, Uruguay. His works on leather problems and defects have been published in international and regional journals. He is currently working as a freelance consultant.

J.M. Morera graduated in Chemistry at the University of Barcelona (Spain) in 1983. He received his PhD degree in Chemistry at the same University in 1994. He received the Master in Tanning Technical Management from the Universitat Politècnica de Catalunya (Spain) in 1999. From 1985 to 2018 he worked as an associate professor at the Universitat Politècnica de Catalunya (Spain). From 2018 to 2020 he worked as an associate professor at the Universitat de Lleida (Spain). Since 2020 he has been working as a full professor at the Universitat de Lleida (Spain). He is mainly involved in the development of cleaner and innovative leather processing methods.

E. Bartolí graduated in Chemistry at the University of Barcelona (Spain) in 1985. He received his PhD degree in Chemistry at the same University in 2000. He received the Master in Tanning Technical Management from the Universitat Politècnica de Catalunya (Spain) in 1999. From 1985 to 2018 he worked as an associate professor at the Universitat Politècnica de Catalunya (Spain). Since 2020 he has been working as an Associate Professor at the Universitat de Lleida (Spain). She is mainly involved in the development of cleaner and innovative leather processing methods.

Rafael Fernández graduated in Chemical Engineering at Polytechnic University of Catalonia (UPC) (Spain) in 2017. He received the Master in Tanning Technical Management from the Universitat Politècnica de Catalunya (Spain) in 2019. He worked in 2018- 2019 at Proyecto Fontanellas y Martí S.L. as a laboratory technician. He is currently working at Malena Engineering as an engineer.

L.F. Cabeza graduated in chemical engineering and industrial engineering at the University Ramon Llull (Barcelona, Spain) in 1993. She received an MBA in 1995 and her PhD in 1996 at the same university. From 1996 to 1998 she was a post-doctoral researcher at ERRC-ARS-USDA (Philadelphia, USA). In 1999 she joined the Universitat de Lleida (Spain), where she created and is leading the GREiA research group. Her research interests are on energy efficiency, circular economy, and social acceptance of technologies.

Murshid Jaman Chowdhury is working as a Senior Scientific Officer in Leather Research Institute, Bangladesh Council of Scientific and Industrial Research (BCSIR), Nayarhat, Savar, Dhaka-1350, Bangladesh. He did my BSc. (Hons.) and MS degree from the department of Applied Chemistry and Chemical Engineering, University of Dhaka, Bangladesh. His research interests in leather tanning, deliming, fat-liquoring and dyeing.

Md. Abdur Razzaq is working as a Scientific Officer in Leather Research Institute, Bangladesh Council of Scientific and Industrial Research (BCSIR), Nayarhat, Savar, Dhaka-1350, Bangladesh. He completed his BSc. (Hons.) degree in Leather Engineering from Institute of Leather Engineering and Technology, University of Dhaka, Bangladesh and MS degree in Applied Chemistry and Chemical Technology from Islamic University, Kushtia, Bangladesh. His research interests in leather tanning, deliming, fat-liquoring and dyeing. His research interests in leather curing, tanning, and fat-liquoring.

Md. Imran Biswas is working as a Research Fellow in Leather Research Institute, Bangladesh Council of Scientific and Industrial Research (BCSIR), Nayarhat, Savar, Dhaka-1350, Bangladesh. He did is BSc. (Hons.) and MSc. degree from the department of Chemistry, Jahangirnagar University, Bangladesh.

Ariful Hai Quadery is a former Director-in-Charge in Leather Research Institute, Bangladesh Council of Scientific and Industrial Research (BCSIR), Nayarhat, Savar, Dhaka-1350, Bangladesh. He completed his BSc. (Hons.) degree in Leather Engineering from Institute of Leather Engineering and Technology, University of Dhaka, Bangladesh and MS degree in Leather Engineering from Northampton University, UK.

Md. Tushar Uddin is working as a Senior Scientific Officer in Leather Research Institute, Bangladesh Council of Scientific and Industrial Research (BCSIR), Nayarhat, Savar, Dhaka-1350, Bangladesh. He completed his PhD degree from the department of Chemistry, Jahangirnagar University, Bangladesh. He also did my BSc. (Hons.) and MSc. degree from the department of Applied Chemistry and Chemical Technology, University of Rajshahi, Bangladesh. His research interests in leather tanning, deliming, fat-liquoring and dyeing.

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Eaglewood Resort & Spa, Itasca, Illinois
June 21-24, 2022

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