THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

April 2014 Vol. CIX, No. 4 *JALCA* 109(4), 99-137, 2014

110th Annual Convention

to be held at the Gideon Putnam Resort Saratoga Springs, New York June 18 - 20, 2014

For more information go to www.leatherchemists.org/annual_convention.asp

ISSN: 0002-9726

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Proceedings, Reports, Notices, and News
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THE JOURNAL OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION (USPS #019-334) is published monthly by The American Leather Chemists Association, 1314 50th Street, Suite 103, Lubbock, Texas 79412. Telephone (806)744-1798 Fax (806)744-1785. Single copy price: $8.50 members, $17.00 non-member. Subscriptions: $175 for hard copy plus postage and handling of $60 for domestic subscribers and $70 for foreign subscribers; $175 for ezine only; and $195 for hard copy and ezine plus postage and handling of $60 for domestic subscribers and $70 for foreign subscribers.

Periodical Postage paid at Lubbock, Texas and additional mailing offices. Postmaster send change of addresses to The American Leather Chemists Association, 1314 50th Street, Suite 103, Lubbock, Texas 79412.

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Development of Alginate-Chitosan Based Biopolymers for Leather Retanning

by

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Abstract

Hides and skins when received in tanneries have closely and firmly packed together bundles of collagen fibers, with elastin and other non-fibrous proteins aiding a dense structure formation. However, in order to enable the easy diffusion of chemicals, a series of pre-tanning operations ensure the opening up of the fiber bundles and the removal of the non-fibrous materials, resulting in a loose structure. A majority of leather consumers often demand properties, which were available on hides and skins, but lost during the pre-tanning operations. One such property is the compaction or firm packing of fiber bundles. While vegetable tanning processes provide for good fullness and firm packing of fiber bundles, the lack of strength and stability against wet heat forces the tanners to adopt chrome tanning. Chrome tanning provides for good inter and intra networking of fibers, but is unable to replenish the firmness found in the original raw material. To overcome this drawback, tanners often resort to the use of a combination of retanning agents in varying proportions. The varying character of these products results in non-uniform and poorer uptake. In this work an attempt has been made to develop syntans from biopolymers such as chitosan and alginate, which could provide fiber compaction to the leather.

Introduction

Leather processing is unique. It often calls for destruction of some of the fantastic properties inherently available in the raw material for ensuring easy diffusion of chemicals and subsequently through a series of processes attempt to restore the same. These properties vary from simpler ones such as look, handle, feel etc. to high-end smarter properties such as ability to adjust to hot and cold conditions at will. While the primary aim of tanning is to provide a desired level of hydrothermal stability, the tanning agents often end-up providing a characteristic feel to the leather. For instance soft, supple, not so full leather with better hydrothermal stability and high tensile strength and good color yield is obtained with chrome tanning. While chrome tanning leaves an empty feel in the leather, firmer fuller character, with much less hydrothermal and physical stability is obtained with vegetable tannage. In terms of wash and perspiration fastness, aldehyde tannages are applicable. If the grain needs deep correction, the choice is chrome-vegetable combination. For nubuck type leather, zirconium retannage, and for shrunken grain leather; syntan-chrome combination tannage is considered.[1]

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Manuscript received October 16, 2013, accepted for publication December 31, 2013.

Even though a large variety of tanning agents are available, chrome tanning continues to be the obvious first choice due to the high stability and strength it provides to the leather. The tanner is often happy to overcome the disadvantages such as an empty or non-compact feel of chrome tanned leathers through retanning with synthetic tanning agents.[2] Utility and fashion market often demand, in addition to shades and colors, a host of properties, which are to be met through appropriate retanning Unfortunately, no single syntan is able to confer all the desired properties of the customer, leading to the tanner employing a number of synthetic tanning agents differing in chemical type. The process of choosing appropriate retanning agents (a combination of at least 3 to 5 proprietary products) is even more challenging when poorer quality raw materials, such as those from ill fed or under-nourished animals is employed. The magnitude of uptake of each of these individual syntans and their overall contribution to the final properties of the leather is often difficult to understand.[4]

An initial survey of the Indian leather chemical industry indicates a much desired need to develop such retanning agents, which can in combination with other proprietary products available in the market meet the needs of providing compaction to the collagen fibre bundles in the hide, especially to those of Indian origin. Such new developments need to adequately address the concerns of the customer ecobenign materials. Modern customer preferences are also towards natural materials and recycled products. This work proposes to develop retanning agents, which can provide for firm, fuller and denser fibre structure from natural products and leather wastes through appropriate grafting with polymers. The developed products would be tested against standard retanning processes or agents employed in Indian leather industry on a wet blue cow as substrate and employing different methods for the determination of compactness of leather.

Materials and Methods

Materials

All chemicals used for leather processing were of commercial grade. Chitosan and the chemicals used for the analysis of spent liquors were sourced from SD Fine Chemicals, India. Sodium alginate was obtained from Loba Chemies Pvt. Ltd.

Preparation of Solutions of Alginate and Chitosan

Sodium alginate solution was prepared by adding 1g of sodium alginate to 100 mL water under constant stirring. The stirring was continued till a homogeneous solution of sodium alginate was obtained. Similarly, chitosan solution was prepared by adding 1 g of chitosan to 100 mL of 2% acetic acid solution under constant stirring, until a homogeneous solution of chitosan was obtained.

Preparation of Various Alginate-chitosan Complexes

Alginate-chitosan complexes were prepared by mixing the solutions of alginate and chitosan in 1:1 proportions. The complex thus formed was stirred for a period of 15 minutes, after completion of stirring; the product was adjusted to different pH conditions with sodium bicarbonate. Products A, B and C were obtained by adjusting the product pH to 9, 6 and 3, respectively. The experiments were performed at 25°C. Alginate-chitosan complex adjusted to pH 9 (Product A), was subsequently added with 0.2 gms. of poly acrylic acid (mol. wt. 2100) and the complex stirred for 30 minutes. Urea of 20, 50 and 100 mg (per gram of alginate) were added to the complex to obtain products D, E and F, respectively and the pH of the final products adjusted to 9.0 using sodium bicarbonate.

Determination of Solid Content

A known quantity of product was weighed in an empty dish and dried at 103°C -105°C for 1 hr as per the standard procedure.[5] Total solids of the products were calculated from the dried weight.

Thermal Analysis of the Developed Products

The samples were fused in a differential scanning calorimetric cell of a Seiko Model SSC 5200 220C (DSC) differential scanning calorimeter. The temperature was calibrated effectively using indium as standard. The heating rate was maintained constant at 6°C/min. The denaturation temperature T_D (°C) of the products was measured under N_2 atmosphere.

FTIR Spectral Studies of the Developed Products

The FTIR (Fourier Transform Infrared) spectra of Products were obtained using KBr disc technique. The products were ground in mortar for 5 mins after drying it for a period of 2 hrs at 80°C. Dilution and homogenisation to 0.01% (W/W) with KBr (Spectroscopic grade) were carried out with additional grinding. The disc was pressed in a hydraulic KBr press. The Transmission FTIR spectrum was then recorded using Perkin – Elmer Spectrum RX IFT – IR system between 400 and 4000 cm^{-1}.

Preparation of Leathers

The wet blue cow hides of Indian origin were chosen as raw material for the manufacture of upper leathers. Wet blue cow sides were sammed and shaved to a uniform thickness of 1.1-1.2 mm and corresponding shaved weight was noted. The chemicals were offered based on the shaved weight. Post tanning process followed for control leathers is given in Table I. The experiments were carried out in a stainless steel drum with 15 rpm.

Physico-chemical Evaluation of the Leather

Samples for various physical tests from experimental and control crust leathers were obtained as per IUP method.[5] Specimens were conditioned at 80±4°F and 65±2% R.H. over a period of 48 hrs. Physical properties such as tensile strength, % elongation at break, were examined as per the standard procedures.[6] Tear strength was examined as per the standard procedure.[7] Measurement of distension and strength of grain by the ball burst test were examined as per the standard procedure.[8]

TABLE I
Process Recipe for Manufacture of Upper Leather from Wet Blue of Thickness 1.1-1.2 mm (Control).

Process/chemicals	% (based on shaved weight)	Duration (minutes)	Remarks
Washing			
Water	100	10	Drained
Neutralization			
Water	150		
Phenol acrylic copolymer Syntan	5	40	
Neutralizing syntan	2	3x15+45	Check for pH 5.0 -5.2, Drained.
Washing			
Water	200	15	Drained
Water	100	15	Drained
Retanning, Dyeing and Fat liquoring			
Water	50		
Acrylic resin	3		
Synthetic fatliquor	1	30	
Phenolic replacement syntan	8		
Melamin condensate	4		
Wattle-GS powder	4		
Dye	2	90	Check penetration
Water	100	20	
Carbohydrate and protein based filling syntan	2.5	20	
Sulphited synthetic fatliquor	6		
Vegetable semi synthetic fatliquor	1	60	
Sulphited fish oil	1		
Wattle- GS powder	1.5	30	
Formic acid	2	3x10+30	
The exhaustion of the bath was checked. Drained. The leathers were set twice, Hook dried, conditioned and staked.			

Assessment of Softness Through Digital Leather Softness Tester

The softness of the leathers was measured using a MSA ST 300 digital leather softness tester supplied by MSA Engineering Systems Limited as per standard procedure.[9] The method permits measurement of softness of leather without defacing the hide. The measurements were performed using a 35 mm ring at 20 ±2°C and with a relative humidity of 65±2% with thickness of leather being 1.2mm. Higher value indicates higher softness. Measurements were carried out on 5 locations within the sampling area and reported as average.

Reflectance and Color Measurements

The principle involves measuring the amount of light reflected from the surface of opaque specimen at wavelengths throughout the visible spectrum as a fraction of that reflected by a white standard identically illuminated. It is known as the reflectance factor. The white standard used should be an absolute one i.e., it should be a perfect reflecting diffuser whose reflectance at every wavelength is 100%. The control and experimental crust leathers made in this study were subjected to reflectance measurements using an Ocean optics UV 2000 spectrophotometer employing an OOIIrrad software instrument. Color measurement parameters *viz*., L, a, b, h and C were recorded using a Lambda 35 instrument for control and experimental crust leathers[10]; where 'a' represents red and green axis and 'b' represents yellow and blue axis; 'h' represents hue and 'C' represents chromaticity.

Hand Evaluation

Experimental and control crust leathers were assessed for fullness, roundness, softness, grain smoothness, grain tightness (break) and general appearance by hand evaluation methods. The leathers were rated on a scale of 0–10 points for each functional property by experienced tanners, where higher points indicate better properties.

Scanning Electron Microscopy Analysis

Samples from control and experimental tanned leathers were cut from the official sampling position[6] from the crust leather. Samples were cut into specimens and coated with gold using an Edwards E306 sputter coater. A Leica Cambridge stereoscan 440 scanning electron microscope was used for the analysis. The grain as well as cross-section was examined under the microscope at varying magnifications.

Evaluation of Extent of Compaction by Comparing the Physical Property of the Belly and Butt

The physical property of the butt and belly are carried out as per standard procedure.[6-8] The result of both is correlated for the evaluation of the compactness.

Weight Ratio

The circular samples were taken from different portion i.e., neck, belly, tail, shank and flank. A sample was taken in a butt portion such that it mass should be greater than the other portion and named it as tight portion. Then the tight portion was X_n and other portion i.e., neck, tail, belly, shank and flank as X_1, X_2, X_3, X_4 and X_5. To calculate the weight ratio X_1, X_2, X_3, X_4 and X_5 are divided by X_n. The weight ratios of the leathers were used to evaluate the compaction.

Apparent Density

Apparent density is the ratio of apparent mass by apparent volume. Here the weight of the sample was taken as mass and the volume of sample was calculated from the radius of the sample and thickness of the sample. By comparing the values, the extent of compaction was measured.

Analysis of Wastewater

Total volume of wastewater generated was determined. Chemical oxygen demand (COD) and total solids (TS) were determined as per standard procedures.[11]

RESULTS AND DISCUSSION

Synthesis of Alginate-chitosan Complexes

A polyelectrolyte complex (PEC) is formed by the association of two or more polymers based on their electrostatic force. For example, a polycation interacts with a polyanion through a proton transfer, resulting in the formation of PEC. Preparation of PEC's using chitosan and a counter pair of polyanion, like an alginate composed of (1-4)-linked β-D-mannuronic acid and α-L-guluronic acid units is reported as an effective technique for preparing separating membranes and microcapsules.[12,13] White precipitates in the chitosan/alginate solutions indicated the formation of a PEC. Solutions of alginate (1%) and chitosan (1%) were mixed in proportion of 1:1, in a magnetic stirrer for a period of 30 min at room temperature. A stable product was formed having a pH of 4.5 and solid content of 16%. The pH has a strong influence on polyelectrolyte functional groups. Three PEC's were prepared at pH 9, 6 and 3 and are termed as product 'A', 'B', and 'C', respectively. The FT-IR spectra of the prepared products are presented in Fig. 1a-c.

A peak at around 1420 cm^{-1} can be seen for all complexes. Intensity of this peak increases from Product C (pH 3) to Product B (pH 6) and decreases a little for Product A (pH 9). This peak is attributed to the amino (NH_3^+) groups of chitosan interacting with the carboxyl ($-COO^-$) groups of alginate. A strong peak at 1750 cm^{-1} is seen in Product C (pH 3). This peak is explained by non-ionization of (-COOH) groups of alginate at low pH values. The peak seen for all complexes at 1560 cm^{-1} explains unreacted ($-NH^3$) groups of chitosan.

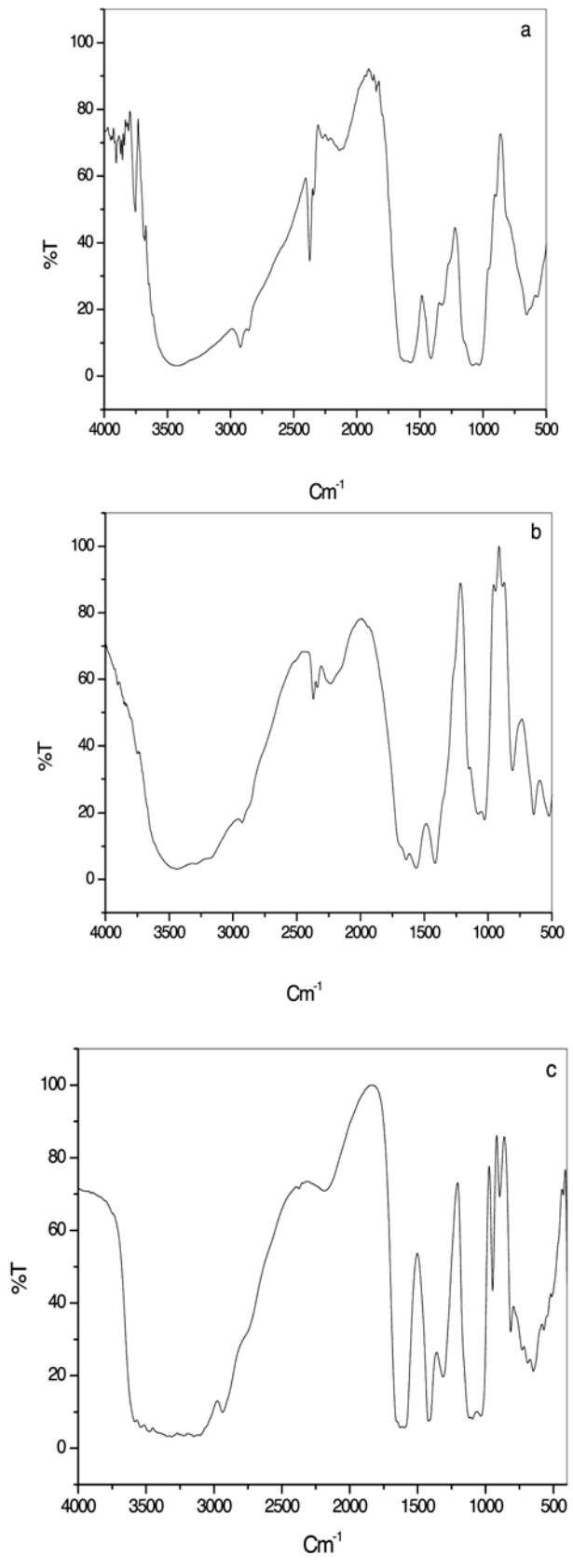

Figure 1. FTIR spectra of a) Product A b) Product B and c) Product C.

A thermogravimetric analysis performed on the Product A (Fig. 2) revealed that with increasing temperature the weight of sample decreases rapidly up to 150°C, slowly in the 150–200°C range. The loss of weight is mainly attributed to the loss of free and bound water. Beyond 200°C the compound appears to be stable up to 1000°C and above this temperature significant weight loss is noticed, which could be due to thermal degradation of the compound.

Three products developed have been used for the retanning of cow wet blue of Indian origin. The process followed for control and experiment is shown in Table I and II. The variation in tensile strength, tongue tear strength, the load and distension at grain crack, as well as softness for the leathers processed using products A, B and C is as presented in Table III. Adequate tensile strength is very important in manufacture of upper leather. The cutting direction had a varying effect depending on the retanning agent used. The load at grain crack was highest for Product A, followed by product C and product B. This effect could be attributed to the greater surface fixation that accompanies with the elevated pH conditions. Product B (pH 6) reduces the distension of grain crack in the ball burst test marginally, when compared to Product A and Product C. The resistance to fracture was highest when Product A was employed, followed by Product B and C, respectively.

Apparent density is an important factor controlling the softness of the leather. It has been shown earlier that apparent density can directly be related to assessment of compaction of fiber weave. Lower apparent density results in softer leathers. This is attributed to the larger unfilled spaces between individual fiber bundles.14 A marginal difference in softness was observed as the retanning process varied, with Product B offering a slightly higher softness than Product A and C. Thus it can be concluded that Product A offered a higher filling of the interfibrillar spaces than Product B and C. Subsequent experiments were carried out with Product A, as it showed better characteristics.

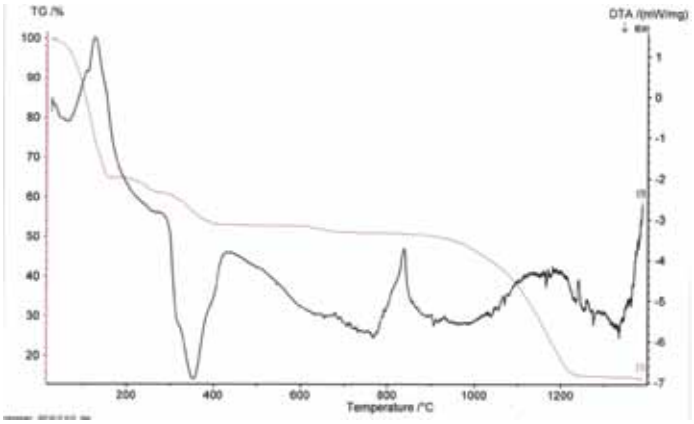

Figure 2. Thermogravimetric spectrum of product A.

TABLE II
Process Recipe for Manufacture of Upper Leather from Wet Blue of Thickness 1.1-1.2 mm (Experimental).

Process/chemicals	% (based on shaved weight)	Duration (minutes)	Remarks
Washing			
Water	100	10	Drained
Neutralization			
Water	150		
Phenol acrylic co polymer syntan	5	40	
Neutralization syntan	2	3x15+45	Check for pH 5.0 -5.2, Drained.
Washing			
Water	200	15	Drained
Water	100	15	Drained
Retanning, Dyeing and Fat liquoring			
Water	50		
Acrylic resin	3		
Synthetic fatliquor	1	30	
Phenolic replacement syntan	8		
Melamine condensate resin	4		
Wattle- GS powder	4		
Dye	2	90	Check penetration
Water	100	20	
Product A*, B, C, D, E or F	2.5	20	
Sulphited synthetic fatliquor	6		
Vegetable base semi synthetic fatliquor	1		
Sulphited fish oil	1	60	
Wattle- GS powder	1.5	30	
Formic acid	2	3x10+30	

The exhaustion of the bath was checked. Drained. The leathers were set twice, hook dried, conditioned and staked.
* A is varied at 2.4, 3.2, 4.0, and 4.8%

Role of Percentage Offer of Product on the Physical Properties Of The Leathers

A pronounced increase in the tensile strength of the leather is observed as the offer of product A varied from 2.4 to 4.8% as shown in Table IV. The resistance to fracture, as measured by the tear strength is observed to be constant over the range of concentrations investigated. There is an increase in the grain crack strength up to an offer of 3.2%. Further increase in concentration of the product to 4.8%, decreased the grain crack strength. This could be attributed to the overloading of grain by the product. Softness seems to be unaltered by the concentration of product offered.

Role of Combining Natural and Synthetic Polyanions and Urea in PEC Formation

Poly (acrylic acid) (PAA) has been chosen as a synthetic polyanion. A chitosan-PAA polyelectrolyte is expected to penetrate into tighter areas like butt, leaving the chitosan-Alg polyelectrolyte to penetrate into the looser areas like belly. When alginate is compounded with urea, the spreading and diffusion of alginate into the leather matrix can be controlled. In this work, the role of urea in enabling a better penetration of the chitosan-Alg polyelectrolyte into the looser areas is being evaluated. Product A complexed with PAA in

TABLE III
Comparison of Physical Properties of Leathers Retanned with Product A, B and C.

Samples	Tensile strength (kg/cm^2)	Tongue tear (kg/cm)	Load at grain crack (kg)	Distension at grain crack (mm)	Softness
Product A	275±5	74±2	51±3	12±1	-3.2
Product B	244±3	60±2	30±1	10±2	-3.8
Product C	273±3	40±2	40±1	12±1	-3.0

TABLE IV
Comparison of Physical Properties of Leathers Retanned with Increased Offer of Product A.

Product A (%)	Tensile strength (kg/cm^2)	Tongue tear (kg/cm)	Load at grain crack (kg)	Distension at grain crack (mm)	Softness
2.4	236±2	71±2	40±2	13±2	-3.3
3.2	305±8	70±3	52±5	12±2	-3.8
4.0	275±3	74±3	51±2	12±1	-3.2
4.8	338±7	67±2	37±3	10±2	-3.1

TABLE V
Comparison of Physical Properties of Leathers Retanned with Product D, E, and F.

Samples	Tensile strength (kg/cm^2)	Tongue tear (kg/cm)	Load at grain crack (kg)	Distension at grain crack (mm)	Softness
Product D	250±1	59±2	47±2	10±2	-5.0
Product E	260±3	59±2	50±2	12±2	-5.2
Product F	296±2	63±2	48±3	12±1	-4.2

combination with urea concentration of 20, 50, and 100 mg (per grams of alginate), referred to as product D, E, and F were prepared. Retanning process as described in Table II has been followed to process the leathers with these products. The physical properties of the leather tanned with Products D, E and F is presented in Table V. As expected at higher urea offer, the tensile strength and tongue tear resistance was improved. The lower distension at grain crack could be attributed to a better filling of the corium-grain junction. The lower softness with Product F could be attributed to a better filling of the interfibrillar portions. This is further substantiated from the apparent density values, which followed the order.

Comparison of Leather Characteristics Between Products A, F and Control

Experimental process as provided in Table II has been employed for comparing the characteristics incorporated by products A and F as against control process employing commercial syntan, specifically aimed at selective filling of looser ends. Left-right comparison method was adopted. The physical properties of the leathers have been compared both at the butt and the belly region of the sides. The sample specimens have been cut exactly at similar positions on the left and right sides of the hide. The results are presented in Table VI. It can be clearly seen that the Product F is better when compared to the control process, in its ability to confer strength to the butt and belly regions in comparison to similar regions of the control leather. The weight ratios and apparent density of different regions of the leather (sides) made from Product A, Product F and commercial syntan are presented in Table VII. It is seen from the table that the weight ratio of belly region is lower as compared to other regions in both control and experimental trials. However, leathers made from Product A exhibited similar characteristics as compared to

TABLE VI
Comparison of Physical Properties of Leathers Retanned with Product A and F as Against Control.

Samples	Tensile strength (kg/cm^2)		Tongue tear (kg/cm)		Load at grain crack (kg)		Distension at grain crack (mm)		Softness
	Butt	Belly	Butt	Belly	Butt	Belly	Butt	Belly	
Product A	275±5	200±2	75±2	70±3	52±2	48±4	10	10.5	-4.7
Product F	296±5	210±3	65±5	58±3	48±1	42±2	11.4	11.9	-4.1
Control	280±4	200±2	62±3	70±2	46±5	43±3	10.2	11.1	-4.7

TABLE VII
Weight Ratio and Apparent Density of Leathers Retanned with Product A and F as Against Control

Samples	Product A		Product F		Control	
Sampling position	Weight ratio	Apparent Density (gm/mm^3)	Weight ratio	Apparent Density (gm/mm^3)	Weight ratio	Apparent Density (gm/mm^3)
Neck	0.94	0.042	0.95	0.048	0.92	0.042
Tail	0.96	0.046	0.95	0.052	0.96	0.049
Belly	0.70	0.042	0.67	0.039	0.77	0.041
Shank	0.89	0.042	0.64	0.044	0.95	0.047
Flank	0.93	0.044	0.81	0.044	0.85	0.045

control leathers. The weight ratios are lower in belly and shank regions for leathers made from product F. The distribution of weight ratio in all the regions is good for the leathers made from Control and Product A. This indicates that Product A is filling up the looser areas thus enabling uniform distribution of the product in the leather to provide the required compaction. However, the apparent density values for all the leather at different regions seems to be equal, except for belly region, where the apparent density is slightly lower. The lower apparent density of the leather means that they may be expected to have larger spaces between individual fiber bundles.

SEM Analysis

The grain surface and cross section from the butt portion and belly portion of the leathers from control and experimental (Product A and F) have been analyzed using Scanning Electron Microscopy (SEM). Grain surface of all samples obtained seems to be clean and appears to be similar (Figures not shown). SEM images of the cross section of all samples obtained from butt and belly portions are provided in Fig. 3 and 4, respectively. The sample from product F shows a compact and regular fiber structure. This could be due to the filling nature of the product. The product A and control samples shows lower compaction of fibre structure compared to product F. The orientation of the fiber structure in the belly region for samples treated with product 'A', 'F' and control are comparable (Fig. 4). However, the product F provides more compaction compared to the other samples. This is in agreement with the above observation.

Hand Evaluation of Leathers

The hand evaluation data for the crust leathers made from Product A, F and control is given in Table VIII. It is observed from the table that the overall rating of leathers made from Product A and Product F are comparable to that of control. Although the leather made from Product A are more fuller and softer, the grain tightness needs to be improved. However, the grain tightness is better in the case of leathers made from Product F. Color measurement results are presented in Table IX. The color values obtained were similar and also the colors are comparable to the naked eye.

A comparison of the physical properties obtained for the butt region as against the belly region of the same cow side reveals interesting results. The differential figures are presented in Table X. The change in tensile strength, tongue tear, grain crack resistance and distension at grain crack were lowest with Product A when compared with Product F. This is possible as the Product F, which contained an alginate and polyacrylic acid in combination with chitosan can penetrate into both butt and belly regions, while Product A, which contains only alginate in combination with chitosan can penetrate into the

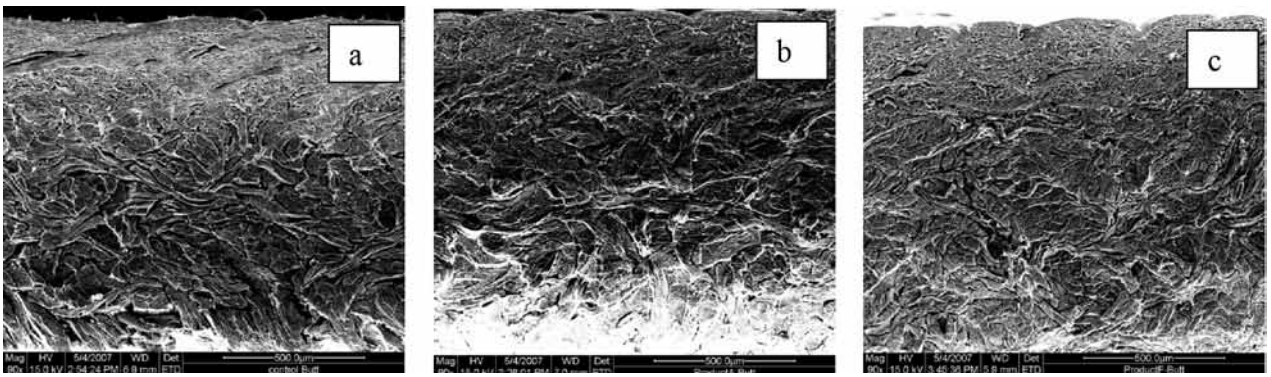

Figure 3. Scanning electron micrographs of cross section of the butt portion of the samples a) Control b) Product A c) Product F.

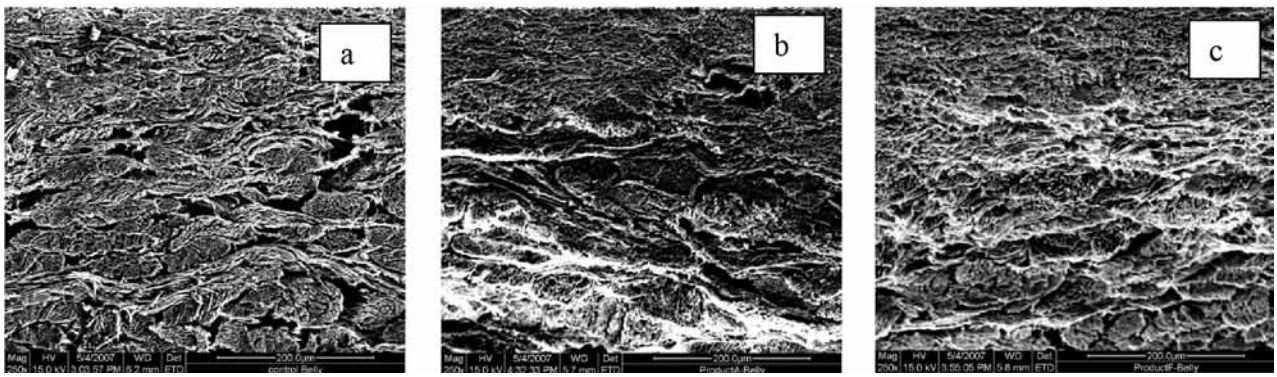

Figure 4. Scanning electron micrographs of cross section of the belly portion of the samples a) Control b) Product A c) Product F.

TABLE VIII
Hand Evaluation of Leathers Retanned with Product A and F as Against Control

Samples	Fullness	Roundness	Smoothness	Softness	Tightness
Product A	8	7	8	8	5
Product F	7	7	6	5	7
Control	6	7	8	7	6

TABLE IX
Comparison of Reflectance Values of Leather Retanned with Product A and F as Against Control.

Samples	L	a*	b*	Hue	C
Product A	22	-2	3	123	3.6
Product F	21	-1	1	45	1.4
Control	25	-4	6	123	7.2

TABLE X
Difference in Butt and Belly Strength Values of Leathers Retanned with Product A and F as against Control Leather

Samples	Tensile strength difference ΔTS (kg/cm^2)	Tongue tear difference (kg/cm) ΔTT	Load at grain crack difference (kg) ΔGC	Distension at grain difference crack (mm) ΔDGC
Product A	75	5	4	0.5
Product F	86	7	6	0.5
Control	80	8	3	0.8

TS: Tensile Strength; TT Tongue Tear Strength; GC: Grain Crack Strength; DGC: Distention at Grain Crack

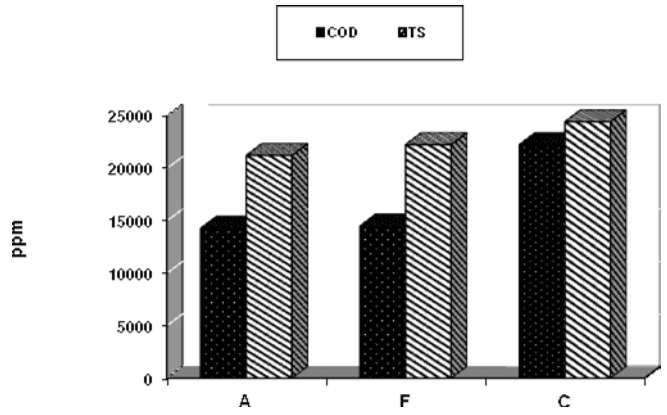

Figure 5. Comparison of amount of chrome, COD and TS for leather retanned with Product A and F as against control.

belly alone, thereby providing strength to the belly, while retaining the properties of the butt region. The study however indicates that it is possible to obtain compact leathers using Product A or Product F.

Environmental Impact of the Processes Studied

The primary objective of this study was to develop a synthetic tanning agent from natural sources, which could be used as a replacement for current day products. In the current context of "leather with care", it is imperative that such products do not add additional load to the environment. It is in this direction that a synthetic tanning agent was developed from natural sources. The environmental impact data has been assessed only for Product A and Product F as these products exhibit

better characteristic leathers. A comparison of the chemical oxygen demand of the wastewater and total solids in the wastewater has been made and is presented in Fig. 5. The COD and TS values are more or less similar. The COD values can be considered as a measure of the uptake of the retanning agent. Based on the results obtained from the strength characteristics, performance analysis, SEM analysis and environmental assessment, it is possible to process leathers with uniform compactness using Product A or Product F.

CONCLUSIONS

In this work, six products have been developed based on biopolymeric materials such as chitosan and alginate for providing compact leathers. Product A and Product F have been screened to have better properties as compared to other products. FTIR studies on various products indicate the complexation between the chitosan and alginate in the products. Incorporation of polyacrylic acid and urea in Product F improves the grain tightness of the final crust leather. SEM analysis indicates better compactness for leather made using Product A as compared to Product F. Butt–belly region comparison is similar for leathers made from Product A and F. Strength characteristics of the leather made from Product A are similar to control leathers. Softness of the leathers made from product A is better and comparable to control, whereas the grain tightness of the leathers made from product F is better. Weight ratios for different regions indicate that the leathers made from Product A are comparable to control leathers thereby providing compact leathers. Apparent density values are similar for all the leathers made from Product A or Product F for different regions except for belly. Weight ratio distribution in different regions for leathers made from control and Product A are better except for the belly indicating uniform distribution of compactness. Environmental assessment indicates that the experimental process, employing Product A or F, gave lower COD and TS as compared to control process. Hence it could be concluded that it is possible to make compact leathers using Product 'A' or Product 'F' prepared from natural materials.

ACKNOWLEDGMENT

The authors thank CSIR for funding under the Supra-institutional Project – S&T Revolution in Leather with a Green Touch (STRAIT) (CSIR-CLRI communication no.:1038).

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Sustainability in Process Innovation: Development of a Green Tanning Process Supported by LCA Methodology

by

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Abstract

As a response to the growing concerns about a variety of environmental issues expressed by public opinion and political bodies, the leather industry needs to support its market by environmental criteria as a guarantee of quality. For this reason, assessment tools as Life Cycle Assessment (LCA) methodology, which allow a more thorough knowledge of the products to the enterprises and can help to guide the environmental policies, are recommended (e.g. EC Directive on Ecologic Labels). The LCA methodology, described in details by the ISO 14000 series, allows the assessment of the environmental impacts due to products, processes, or services, by the identification of the inputs (e.g. energy and material consumption) and outputs (e.g. waste and pollutant production) streams exchanged by the process with the environment (i.e. from raw materials procurement to waste streams disposal). The application of LCA as tool for integration of sustainability aspects in process design and development is gaining wider acceptance and methodological development. In this study, the life cycle modeling was used to support the development of a novel tanning process based on the use of a new class of tanning agent produced from renewable resources (e.g. glucose). The experimental activity performed to investigate the technical feasibility of the innovative tanning cycle was supported by the modelling of the process using the LCA methodology in order to assess the environmental performance of the leather production cycle. Therefore, an LCA analysis was performed in order to compare the glucose-tannage process with the traditional one from an environmental point of view.

Introduction

As a response to the growing concerns about a variety of environmental issues expressed by public opinion and political bodies, the leather industry needs to support its market by environmental criteria as a guarantee of quality. Since sustainability is a global concept, this inevitably calls for a system-wide analysis. A system perspective is at the core of the Life Cycle Assessment (LCA) approach, which can provide valuable support in the sustainability evaluations, as demonstrated by the numerous environmental policies at European level (e.g. EC Directive on Ecologic Labels), based on the life cycle concept. The LCA methodology, described in details by the ISO 14000 series, allows the assessment of the environmental impacts due to products, processes, or services, by the identification of the input (e.g. energy and material consumption) and output (e.g. waste and pollutant production) streams exchanged by the process with the environment (i.e. from raw materials procurement to waste streams disposal). During the early years of LCA, the methodology was mostly applied to products but recent literature suggests that it also has potential as an analysis and design tool for chemical processes.[1,2] LCA could be used in several contexts. These include use in process design for comparison and selection of options;[3] in business planning for identifying weak links in a processing chain or in comparing processes with those of business competitor; at the research and development phase of a process,[4] in guiding process evolution[5].

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Manuscript received July 9, 2013, accepted for publication December 23, 2013.

Besides, during the evolution of the methodology, a number of related applications emerged, including its use as basis to communicate the overall environmental performance of the products to stakeholders. Specific standards are available for LCA-based environmental labels and declarations. The International Standards Organization (ISO) has classified the existing environmental labels into three typologies—types I, II, and III—and has specified the preferential principles and procedures for each one of them (ISO 14021, ISO 14024, and ISO 14025). An Environmental Product Declaration (EPD), also referred to as type III environmental declaration, is a standardized (ISO 14025) and LCA-based tool to communicate the environmental performance of a product[6]. There are a number of requirements for how the LCA should be performed to be used as basis for an EPD. They are concerned on detailed specifications on how to model the product system in the LCA, what to include, what data to use, which environmental indicators to report, etc. These requirements are developed for different product groups by the industry and are referred to as Product Category Rules (PCRs). The aim of the PCRs is to achieve comparability in results between different producers of the same product. And as such, the PCRs are valuable and useful as basis for any type of LCA to be used in external communication of results. Recently, the PCR for the assessment of the environmental performance of "Finished bovine leather" are established.

In this study, the life cycle modeling was used to support the development of an innovative tanning process based on the use of a new class of tanning agent produced from renewable resources (e.g. glucose). From the pilot scale experimental tests, the novel process by using glucose as tanning agent appears feasible leather processing, from the technical point of view, to produce high quality bovine upper leather. Results have shown that the finished glucose-tanned leather were comparable to the conventional chrome-tanned in terms of mechanical and technical properties.

Life cycle modeling was used to support the development the novel tanning process by assess the environmental performance associated to the whole production cycle. Therefore, the LCA methodology was applied in order to compare the novel process with the traditional one from an environmental point of view. The LCA study was performed in according to the Product Category Rules defined for the EPD system.

METHODS

This study was performed using a methodological framework based on the International Organization for Standardization (ISO) recommendations (UNI EN ISO 14040 and 14044). According to the ISO 14044, LCA methodology consists of four phases: goal and scope definition, inventory analysis, impact assessment and interpretation. In the goal and scope definition are defined the objectives of the study, the functional unit (i.e. the reference unit to which the inputs and outputs are related), the boundaries of the system (i.e. the extension of the study), and the impact assessment methodologies. The inventory analysis involves data collection for all the activities in the studied system: raw materials (including energy carriers), products, and solid waste and emissions. This step includes calculation of the amount of resource use and pollutant emission of the system in relation to the functional unit. The impact assessment phase assigns the inventory results to impact categories and quantifies the system potential contribution to different environmental impacts.

Process Description

The semi-industrial scale tanning runs were conducted in a stainless steel drum (1.2 m diameter, 0.8 m length) by using heavy calf hides (8-12 kg) after the pickling stage (pH 2.6). In each run, the hides were divided into two sides: one side was conventionally tanned with chrome; the other side was tanned according to the innovative recipes (see Tables I and II). After tannage, the two halves followed a retannage/dyeing-fatliquoring cycle to obtain crust leathers currently used by the tannery to produce upper leathers.

Table III reports the results of the physical and mechanical tests of the crust leathers obtained. The results of the assessment of the technical properties of the innovative crust leathers, in comparison with the conventionally chrome tanned leather, are reported in Table IV. A conventional scale of grades ranging from 1 (worst performance) to 5 (best performance) has been used. The novel crust leathers comply very well with the mechanical standards required for high quality bovine upper leather.

Goal Definition and Functional Unit

The main objective of this LCA was to compare the environmental potential impacts of two tanning processes. The traditional chrome-tanned leather was compared to novel leather production based on the use of a new class of tanning agent produced from renewable resources (e.g. glucose). The scope is to include all-important activities of the leather processing, i.e. covering raw materials acquisition and materials production.

Based on Product Category Rules of the international EPD System, the functional unit was set equal to the production of 1 m^2 of "finished bovine leather", intended as a finished product of the tanning sector and ready to become an input as a semi finished good for further transformation in various manufacturing sector. The leather can be used as a semi finished good for different kinds of final products (for example furniture, clothing, footwear etc.). Since the application of finished bovine leather in final consumer products varies

substantially, no specific function has been defined for the product. Therefore, the use phase was not included in the analysis and a cradle-to-gate system was considered. Figure 1 shows the phases included in the analysis. According to the PCRs, the system boundaries include the main flow related to the leather processing: agriculture, cattle raising, slaughtering and tanning. As noted above, since no specific function has been defined for finished leather, the use phase and the waste treatment phase are omitted. The construction of facilities, including the machinery, electrical installation etc., were excluded from the system and only the operation stages were taken into account in the analysis.

Inventory Analysis

The environmental load was calculated in relation to the functional unit, and the inventory results are evaluated and distributed into the life cycle stages. The aggregated data collected for modeling the systems were derived from the experimental tests performed to explore the technical feasibility of the novel tanning cycle. The needed equipment and electricity quantities were calculated in relation to treatment time of the hides in the various stages of the process. Inventory data for the background system (production of chemicals, electricity, lorry transport, etc.) were based on average technology data from the Ecoinvent 2.2. Database.

As most industrial processes yield more than one product, it is necessary to allocate the burdens caused by these processes (resource consumption and emission) to all the products. As defined in PCRs, in this study a mass allocation procedure to rawhide of the impact of agriculture, cattle raising and slaughtering was applied. For example, in the slaughtering phase the allocation factor for raw hides is 7% (i.e. only 7% of the environmental burdens produced upstream of the skinning operation are allocated to hides).

Impact Assessment Method

The study was carried out by using SimaPro 7.3 software (Pré Consultants). To conduct an LCIA (Life Cycle Impact Assessment), it is necessary to select an impact assessment methodology, which regroups the different characterization models for each impact category. These characterization models allow the calculation of characterization factors, which express the measured substance's strength relative to a reference substance.

Among the different methods available in the software, the ReCiPe endpoint and midpoint (hierarchist version) methods were used. An endpoint method was used for the impact assessment in order to achieve maximal agreement with the comparative and management-oriented objectives of the study. Endpoint indicators describe the integrated damage of the components from the inventory, in contrast to midpoint indicators that address effects only. For global warming, a typical midpoint indicator would be the effect of radiative forcing (global warming potential), whereas the endpoint approach would assess the human and environmental damage based on radioactive effects. Use of endpoint indicators facilitates the interpretation of the results and allows integration of environmental burdens to a single score indicator (the midpoint characterization factors are multiplied

TABLE I
Recipe of the semi-industrial scale tanning runs with chrome (the dosages are reported as wt.% on the fleshed hide weight).

Pickle float	50%	
Chromium sulfate (26/33)	4.5%	30 min
Antibacterial	0.2%	1hr
Sodium acetate	0.6%	1 hr
Basic Chromium sulfate (26/33)	4.5%	4 hr
MgO basifying agent	1.0%	9 hr
Overnight		
Drain		
Horse up		48 hr
Pressing and shaving		

TABLE II
Recipe of the semi-industrial scale tanning runs with glucose (the dosages are reported as wt.% on the fleshed hide weight).

Pickle float	50%	
Sodium formiate	1.5%	
Liquid glucose (43°Bé)	10%	2 hr
Liquid glucose (43°Bé)	15%	8 hr
Hydroxysulphonic syntan	2%	2 hr
Overnight		
Drain		
Horse up		48 hr
Pressing and shaving		

with a damage factor to obtain the endpoint characterization values). ReCiPe uses three main damage categories: human health, ecosystems and resources. Human health includes climate change, ozone depletion, human toxicity, photochemical oxidant formation, particulate matter formation, and ionising radiation (expressed in disability adjusted life years, DALY). Ecosystems include climate change, terrestrial acidification, freshwater and marine eutrophication, terrestrial, freshwater and marine ecotoxicity, agricultural and urban land occupation, and natural land transformation (expressed in species·yr). Resources include metal depletion and fossil depletion, expressed in $.

RESULTS AND DISCUSSION

The results of the life cycle assessment of the traditional leather production (chrome-tanned) at endpoint level are reported in Figure 2. Regarding the three damage categories (human health, ecosystems and resources), the graphic highlights the environmental impact of the tannery compared with the others activities related to the leather production (agricultural phase, cattle raising, slaughterhouse are included in the *raw hides* block). The contribution to Ecosystems damage category is remarkably higher for the activities associated with the calf hides production in relation with the agricultural stage and cattle raising. The agriculture-related emissions are caused mainly by fertilizer use and production. The use of fertilizers causes N_2O emissions, which contribute to Climate change category included in Ecosystems damage category, and nitrate emissions in water, which contribute to Eutrophication and Human Toxicity categories. Also the emission of methane from the cattle raising causes the main impacts and contributes largely to Climate Change and Photochemical oxidant formation categories. This result is especially notable taking into account the fact that only 7% of the impacts generated in these phases have been allocated to leather production.

TABLE III

Physical tests results of the crust leather.

	Shrinkage temperature (°C) UNI EN ISO 3380 method	Tearing load (N) UNI EN ISO 3377/2 method	Grain distension (mm) UNI 11308 method
Traditional leather production	94	151.3	9.6
Novel leather production	92	154.4	9.4
		UNI 10594 guidelines: 30÷80[(1)]	UNI 10594 guidelines: ≥ 7

[(1)]depending on use

TABLE IV

Technical properties of the crust leather.

	Traditional leather	Novel leather
Color homogeneity	4	4
Color yield	4/5	3/4
Roundness	4	3
Fullness	4	3
Wrinkle	4	4
Hand	4	3
Grain quality	4	4

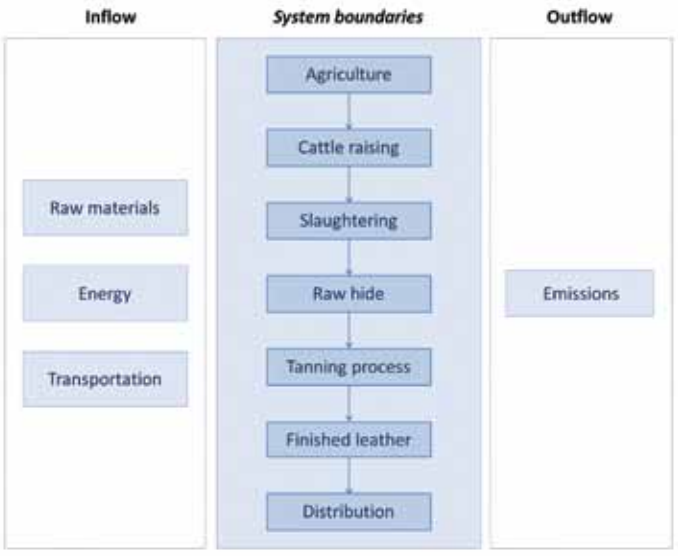

Figure 1. Life cycle flow diagram of the studied system.

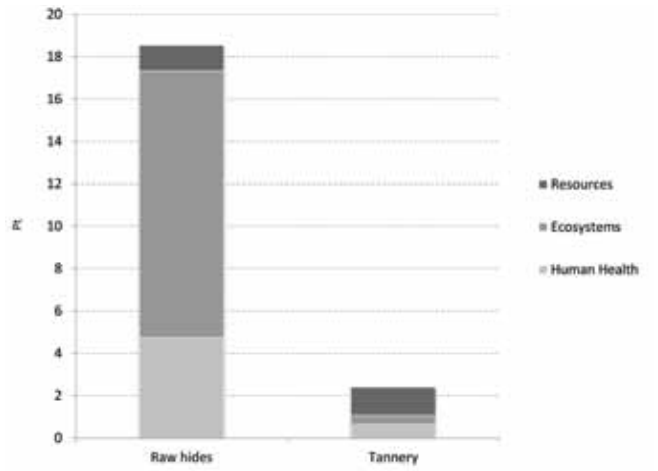

Figure 2. Results of the life cycle assessment of the chrome tanned leather at endpoint level.

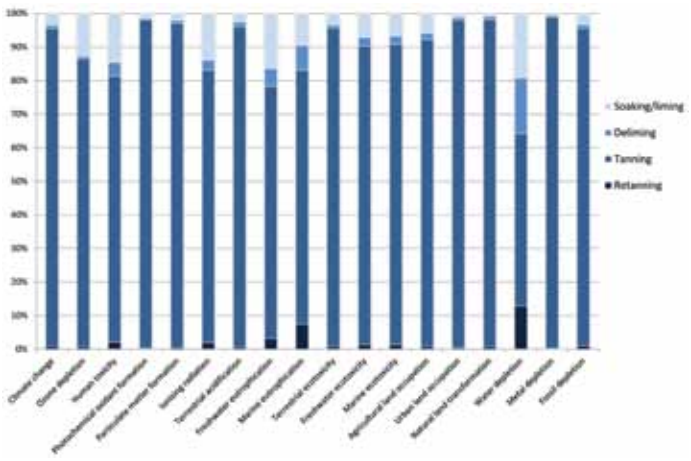

Figure 3. Contribution of subsystems of the chrome-tannage cycle to each impact category.

TABLE V
Midpoint results per impact categories.

Impact Category	Unit	Traditional leather production	Novel leather production
Climate change	kg CO_2 eq	$1.93 \cdot 10^{2}$	$1.75 \cdot 10^{2}$
Ozone depletion	kg CFC-11 eq	$1.63 \cdot 10^{-5}$	$1.37 \cdot 10^{-5}$
Human toxicity	kg 1.4-DB eq	3.33	1.39
Photochemical oxidant formation	kg NMVOC	$3.26 \cdot 10^{-1}$	$1.89 \cdot 10^{-1}$
Particulate matter formation	kg PM10 eq	$3.45 \cdot 10^{-1}$	$3.07 \cdot 10^{-1}$
Ionising radiation	kg U235 eq	2.72	1.21
Terrestrial acidification	kg SO_2 eq	2.25	2.16
Freshwater eutrophication	kg P eq	$5.63 \cdot 10^{-3}$	$4.05 \cdot 10^{-3}$
Marine eutrophication	kg N eq	2.64	2.63
Terrestrial ecotoxicity	kg 1.4-DB eq	$3.26 \cdot 10^{-3}$	$6.35 \cdot 10^{-4}$
Freshwater ecotoxicity	kg 1.4-DB eq	$8.92 \cdot 10^{-2}$	$2.28 \cdot 10^{-2}$
Marine ecotoxicity	kg 1.4-DB eq	$9.64 \cdot 10^{-2}$	$2.38 \cdot 10^{-2}$
Agricultural land occupation	m2a	$2.25 \cdot 10^{2}$	$2.24 \cdot 10^{2}$
Urban land occupation	m2a	$2.07 \cdot 10^{-1}$	$1.26 \cdot 10^{-2}$
Natural land transformation	m2	$6.61 \cdot 10^{-3}$	$6.38 \cdot 10^{-4}$
Water depletion	m3	$2.59 \cdot 10^{-1}$	$1.59 \cdot 10^{-1}$
Metal depletion	kg Fe eq	5.61	$1.86 \cdot 10^{-1}$
Fossil depletion	kg oil eq	$1.41 \cdot 10^{1}$	7.89

TABLE VI
Disadvantage factors per impact categories.

Impact Category	Unit	Traditional leather production	Novel leather production
Climate change	kg CO_2 eq	1.10	1.00
Ozone depletion	kg CFC-11 eq	1.19	1.00
Human toxicity	kg 1.4-DB eq	2.40	1.00
Photochemical oxidant formation	kg NMVOC	1.73	1.00
Particulate matter formation	kg PM10 eq	1.12	1.00
Ionising radiation	kg U235 eq	2.25	1.00
Terrestrial acidification	kg SO_2 eq	1.04	1.00
Freshwater eutrophication	kg P eq	1.39	1.00
Marine eutrophication	kg N eq	1.00	1.00
Terrestrial ecotoxicity	kg 1.4-DB eq	5.13	1.00
Freshwater ecotoxicity	kg 1.4-DB eq	3.91	1.00
Marine ecotoxicity	kg 1.4-DB eq	4.06	1.00
Agricultural land occupation	m2a	1.00	1.00
Urban land occupation	m2a	16.41	1.00
Natural land transformation	m2	10.37	1.00
Water depletion	m3	1.63	1.00
Metal depletion	kg Fe eq	30.20	1.00
Fossil depletion	kg oil eq	1.78	1.00

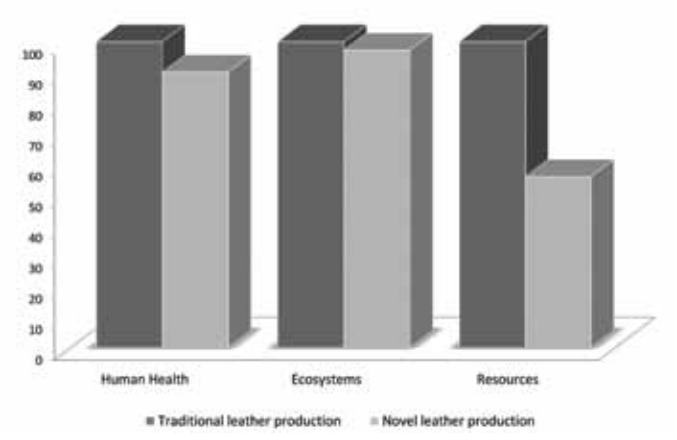

Figure 4. Comparison of the environmental impacts associated with the two tanning process at endpoint level.

Figure 3 shows the results of a contribution analysis performed to reveal the most important contributing stages for the chrome-tanning cycle. As it can be seen, the tannage phase accounts for most of the whole environmental impact. This result is related to chromium content of the wastes (solid wastes and wastewaters) and also its manufacturing process. Therefore, the substitution of chromium salts with tanning agents having a lower environmental burden in relation with its use (pollutants content of the exhaust bath) and its production can remarkable reduces the impacts of the tannery.

Table V lists the parameter values obtained from the life cycle impact assessment of the two tanning processes, which are used to calculate the disadvantage factors reported in Table VI.

The disadvantage factors are calculated by dividing the higher value by the lower value, in order to highlight how many times a process causes more environmental burdens compared to the other one[7].

The results show that the potential environmental loads for traditional tanning process are higher than the burdens associated to glucose-tanned leather production. As noted above (see Figure 3), the main contribution to environmental impact of hides processing is related to use of chromium salts, therefore the use of glucose instead chromium sulphate reduces the loads of the tannery. This result indicates that the environmental advantage in the novel leather cycle outweigh the costs to the environment in the form of greenhouse gas emissions, particle emissions, use of limited resources, etc. in the traditional chrome-tanned leather production, although the cultivation activities and manufacturing process associated to glucose production were considered. These phases contribute mainly to categories included in the Ecosystem category damage. So the potential effects on ecosystem are very similar for the two-system production, as shows in Figure 4. On the other hand, it must be taken into account that the potential damage on ecosystems is strongly affected by the agricultural phase.

CONCLUSIONS

A comparison of the environmental performance of two leather manufacturing processes was carried out. An innovative tanning process based on the use of a new class of tanning agent produced from renewable resources (e.g. glucose) was compared to the traditional chrome-tanned leather production by using the LCA methodology. From the pilot scale experimental tests, innovative process by using glucose as tanning agent appears a feasible leather processing, from the technical point of view, to produce high quality bovine upper leather. Results have shown that the finished glucose-tanned leather is comparable to the conventional chrome-tanned in terms of mechanical and technical properties. Life cycle modeling was used to support the development the novel tanning process by assess the environmental performance associated to the whole production cycle in view of the application of this new tanning process at industrial scale.

The results of the impact assessment of the chrome tanned leather underline that the main potential impact is associated with the rawhides production in relation with the agricultural stage and cattle raising rather than with the tanning phases. The contribution analysis of the stages reveals that the main contribution to environmental impact of hides processing is related to use of chromium salts. The use of glucose instead chromium sulphate reduces remarkably the environmental loads of the tannery, as highlighted from the results of the comparative analysis at midpoint and endpoint level. Then the outcomes obtained indicate that the novel leather production is a promising alternative to the traditional process to overcome the ever-increasing environmental constraints.

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New Challenges in Chrome-free Leathers: Development of Wet-bright Process

by

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Abstract

The aim of the present work was to develop a new tanning process (wet-bright) that produces perfectly white leather meeting all of the requirements for many kinds of articles, such as automotive, garment and shoe upper. This new process gives leather that is free of chromium, aldehydes, aldehyde precursors and organic solvents. It is the application of a new system based on a product designated Tanfor T™ from the manufacturer Kemira ChemSolutions. When compared to existing traditional wet leather processes, there are economic and environmental advantages resulting from the use of this new system. Also, the mineral character of the new product system offers leathers with high dye affinity; thus enabling very bright colors in all leather applications. We believe this leather offers such perfect dyeing properties because of the brilliant whiteness of the wet-bright intermediate substrate.

Introduction

About 85% of the world's leather is chrome tanned. Chrome tanning has a strong impact on the environment due to its potential to pollute wastewater and the difficulty to eliminate the solid wastes that contains chrome. A great variety of work has been carried out in order to minimize these impacts, such as; recycling of pickle-tanning floats, management of solid waste containing chrome, and using processes with high-exhaustion floats, etc.[1-4]

To reduce the negative environmental impact of the chrome tannage, wet-white tanning is increasingly used. As reported by G. Wolf *et al*., wet-white in the strict sense of the term is taken to be completely free of heavy metals and aluminum salts.[5] Wet-white leathers mostly consist of aldehyde-based products, oxazolidine and/or phosphonium compounds.[6,7] This implies using products which could be harmful to human health. However, the term wet-white may also be applied to leathers that are free of chrome but which may be tanned with aluminum, titanium or zirconium salts.[8] In the present work, we present a new process with the aim of obtaining leather free of chromium, aldehydes, aldehyde precursors and organic solvents.

This new system applies the product Tanfor T™ (from Kemira). The product and its processes are based on a mineral tanning using compounds from aluminum, silicon and natural polycarboxylic acids. It was launched at the 2012 Tanning Tech in Bologna, Italy. It is formulated from environmentally friendly components that are used in water treatment, consumer household products and are partially biodegradable.[9]

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Manuscript received November 6, 2013, accepted for publication January 30, 2014.
Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the American Leather Chemists Association.

MATERIALS AND METHODS

This study was conducted in two stages:

- 1st stage. To establish the tanning mechanism of the new system.
- 2nd stage. To study the viability of the new system for use as a universal tanning system meeting all of the requirements for shoes, automotive and garments.

Material

The tests were carried out by using pickled hides at pH 3.2. Two types of tannage were compared: chrome tanning (Table I) and the new system using Tanfor T™ (Table II).

Tanfor T™ , it is designed as a two-component system:

i) Tanfor T™ -A is the tanning agent based on aluminum-silicon compounds. It is stable only in a certain pH range. At pH values above their stability range, the mineral salts will precipitate. At low pH, they are fully soluble, giving water clear solutions without signs of turbidity. Just below the maximum pH value of the stability range, a transition range is found where colloidal aggregates are formed. It is the colloidal aggregation state that is relevant for mineral tanning.[10]

ii) Tanfor T™-B is a self-basifying agent, self-buffering basic component of the Tanfor T™ tanning system, with a very high content of tanning active material.

The wet-bright intermediate that is obtained with Tanfor T™ is very cationic, which is a good and ideal substrate for anionic post tanning formulations.

Methodology

In order to determine the quality of the leathers and compare both systems, we carried out the physical tests set up by the IULTCS, which allowed us to assess the ability of the leathers to withstand the wear and tear of automotive upholstery, garment and shoe upper. The wet-end formulations used for each of the articles are shown in Table III, IV and V.

The following official methods were used to this end:

- IUP 6 Measurement of tensile strength and percentage elongation (in accordance with EN ISO 3376).
- IUP 8 Measurement of tear load (in accordance with EN ISO 3377-2).
- IUP 9 Measurement of distension and strength of grain by the ball burst test (in accordance with EN ISO 3379).
- IUP 16 Measurement of shrinkage temperature up to 100ºC (in accordance with EN ISO 3380).
- IUP 46 Measurement of fogging characteristics (in accordance with EN ISO 17071).
- IUF 402 Color fastness of leather to light: Xenon Lamp (in accordance with EN ISO 105-B02).
- IUF 450 Color fastness to cycles of to-and-fro rubbing (in accordance with EN ISO 11640).

TABLE I
Wet-Blue tanning formulation (on pickled hides).

Tanning	Wet-Blue	
Water	50%	T = 25ºC
NaCl	5%	rotate - 10' ºBé=8.0 pH = 3.1
Chrome salt 33º Schorlenmeyer	2%	rotate – 60'
Chrome salt 66º Schorlenmeyer	5.5%	rotate – 2 h
MgO	0.3%	rotate – 6 h Overnight pH = 3.8

Rest (24 h), drain, shave and weigh, neutralize (pH = 5) and retannage, dyeing, fatliquoring.

TABLE II
Wet-Bright tanning formulation (on pickled hides).

Tanning	Wet-Blue	
Water	50%	T = 25ºC
NaCl	5%	rotate - 10' ºBé=7 pH = 3.3
Tanfor T-A	4%	rotate – 3 h
Tanfor T-B	2%	rotate – 2 h
Tanfor T-B	2%	rotate – 2 h Overnight pH = 4.4

Rest (24 h), drain, shave and weigh, neutralize (pH = 5) and retannage, dyeing, fatliquoring.

TABLE III
Wet-end formulation for automotive.

Phase	°C	%	Product	Time	Remarks
Washing	30	200	Water	10’	
					Drain
Neutralising	30	200	Water		
		0.4	Sodium formiate		
		0.9	Sodium bicarbonate	120’	pH=5.0
Retanning		10	Basyntan DLXN	30’	
		5	Tara	30’	
		2	Relugan RE	40’	
		10	Basyntan DLXN	30’	
		5	Tara	30’	
Dyeing		1	Beige A	240’	
				Aut night	Through cut
		1	Formic acid (1:10)	60’	pH=3.8
					Drain
Washing	50	200	Water	15’	
					Drain
Fatliquoring	50	200	Water		
		4	Lipsol MSG		
		8	Lipoderm licker A1	60’	
		1.5	Formic acid (1:10)	30’	pH=3.2
					Drain
Washing	40	200	Water	10’	
					Drain

Rest on horse 24h
Setting-out, drying, conditioning, staking and milling

TABLE IV
Wet-end formulation for shoe-uppers.

Phase	ºC	%	Product	Time	Remarks
Washing	35	200	Water		
		0.4	Acetic acid (1:5)	20’	
					Drain
Neutralising	35	150	Water		
		1.5	Sodium formiate	20’	
		1.0	Sodium bicarbonate		
		2	Sellasol NG liq.	120’	pH=5.2
Retanning		3	Relugan RE	40’	
		8	Mimosa		
		3	Basyntan D		
		2.5	Brown HG	120’	Through cut
					Drain
Washing	50	200	Water	20’	
					Drain
Dyeing	50	100	Water		
		0.7	Brown HG (1:5)	20’	
		0.8	Formic acid (1:10)	10’	pH=3.5
		0.3	Brown HG (1:5)	20’	Drain
Fatliquoring	50	100	Water		
		3	Trupon KIII		
		1.5	Truponol IMP		
		1	Trupon PB	60’	
		1.5	Formic acid (1:10)	30’	pH= 3.3
					Drain
Washing	40	200	Water	10’	
					Drain

Rest on horse 24h
Setting-out, vacuum drying, air drying, conditioning and staking

TABLE V
Wet-end formulation for garment.

Phase	ºC	%	Product	Time	Remarks
Washing	35	200	Water		
		0.5	Eusapon OD	20’	
					Drain
Retanning	35	200	Water		
		4	Tannesco HN gran.	60’	
		1.5	Sodium formiate	60’	pH= 4.2
					Drain
Neutralising	35	150	Water		
		1	Sodium formiate	20’	
		1.7	Sodium bicarbonate	2 x 15’	
				60’	pH= 6.2
					Drain
Dyeing	35	70	Water		
		2	Coralon OT		
		3	Blue ACL	60’	Through cut
Fatliquoring	55	130	Water		
		4	Derminol OS1		
		4	Trupon DB 80		
		1	Truponol IMP	60’	
		3	Relugan RE	45’	
		2	Formic acid (1:10)	2 x 15’	
				30’	pH= 3.7
					Drain
Washing	40	200	Water	10’	
					Drain

Rest on horse 24h
Setting-out, drying, conditioning, staking, wheeling, milling and straining

Also, the systems' potential to pollute wastewaters was assessed by analyzing the following parameters: Electrical Conductivity (µ/cm), Suspended solids (mg/L), COD (mg/L), N Kjeldahl (mg/L), Chromium (mg/L).

RESULTS AND DISCUSSION

The first step of this study established the tanning mechanism of the new system and the best conditions to apply Tanfor T™. Since it is a mineral system, application principles like those for chromium were used. Similar to salts of chromium (III) and other mineral compounds, the aluminum-silicon compounds that are the active tanning compound of Tanfor T™ are stable only in a certain pH range. At values above their stability range, the mineral salts will precipitate. At low pH, they are fully soluble, giving water clear solutions without signs of turbidity. Just below the maximum pH value of the stability range, a transition range is found where colloidal aggregates are formed. Colloidal aggregates are stable and will not precipitate, but are larger than the single molecule from which they are formed. It is this colloidal aggregation state that is relevant for the mineral tanning attribute of this system.

In order to formulate an effective tanning system around these aluminum-silicon compounds, Tanfor T™ was developed as a 2-component system. Tanfor T™-A was formulated such that the float pH was around 3.5 when starting from a pickle pH 3.2. At pH 3.5, the hydrodynamic radius of the colloidal aggregates was found to be very small, well below the desired colloidal dimensions. These small particles did not react with collagen; but allowed for a fast and an unhindered penetration through the cross section.

Tanfor T™ -B was formulated such that a pH equal to or higher than 4.2 was reached as an overnight value. At this pH, the aluminum-silicon compounds bind to the collagen matrix. Also, the aluminum-silicon compounds will aggregate which creates bridges between the collagen fibers. After dosing Tanfor T™ -B, the pH in the hide will increase more slowly than in the float. This slowed the locking reaction, which allowed the aluminum compounds of Tanfor T™ -B to also penetrate deeply into the collagen matrix, without excessive reaction on the surface or loss of material in the float.

Once the optimal working conditions were established, the aim of the second stage of this study was to assess whether the leathers made this new Tanfor T™ system had a variety of performance advantage over chrome-tanned leather.

Figure 1 and Figure 2 show the physical tests carried out on the tanned leathers.

As can be seen in both graphs, wet-bright leathers gave similar results like those for wet-blue. Wet-bright leathers showed slightly lower values in both tear load (IUP 8) and in shrinkage temperature (IUP 16) as compared with those obtained for wet-blue leather. But; wet-bright leathers gave a low value in Fogging test (IUP 46). This test measures the amount of volatile compounds, which has been released when high temperatures are achieved. Specifically, wet-bright leather gave a reduction of 8% versus wet-blue.

Another characteristic of wet-bright is that it did not deliberately contain chromium. Table VI shows the comparison of pollution in wastewaters between the processes due to wet-blue and wet-bright.

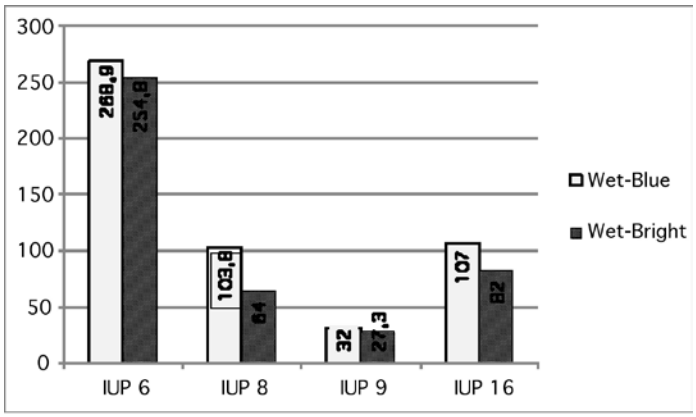

Figure 1. Physical tests.

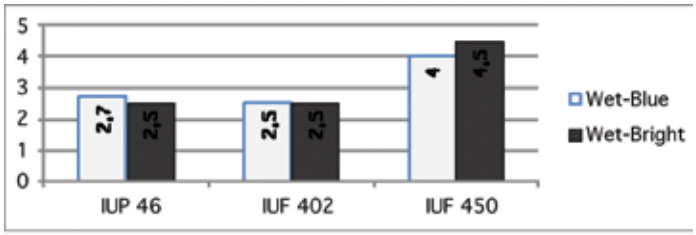

Figure 2. Physical tests.

TABLE VI
Comparison of pollution in wastewaters.

Test	Wet-Blue	Wet-Bright
Conductivity (µS /cm)	85966	101596
Suspended solids (mg/L)	1173	452
COD (mg/L)	9300	3800
N – Kjeldahl (mg/L)	470	165
Chromium (mg/L)	3219.0	No detectable

Chrome tanning is one of the most polluting processes in leather industry mostly due to the presence of chromium in the resulting wastewaters. Again wet-bright showed the following advantages versus wet-blue. Specifically, wet-bright reduced COD by 60%, reduced suspended solids by 61% and reduced nitrogen by 65%. And most important, wastewater did not contain chromium.

Once the tanning mechanism of the new system was established, we studied the viability of the new system as a universal tanning system meeting all of the requirements for shoes, automotive, and garments.

Figure 3 and Figure 4 show the physical tests carried out on the crust leathers (i.e. after the post-tanning processes).

As can be seen in both graphs, wet-bright leathers again gave results like those obtained for wet-blue. Only minor retanning and fatliquoring adjustments were required compared to wet-blue. Thus, we believe that wet-bright processes and their leather qualify as a universal tanning system meeting all of the requirements for shoes, automotive and garments.

Table VII shows the comparison of pollution parameters in wastewaters between the post-tanned wet-blue and the post-tanned wet-bright.

As can be seen in Table VII, wet-bright showed again an advantage over wet-blue. Specifically, wet-bright reduced COD by 40% versus wet-blue, reduced suspended solids by 32%, and reduced nitrogen by 31% in the automotive leathers. A reduction of 53% in COD, a reduction of 17% in suspended solids and a reduction of 18% in nitrogen was obtained in wet-bright shoe upper leathers compared to wet-blue. And wet-bright reduced COD by 7% in versus wet-blue, reduced suspended solids by 33%, and reduced nitrogen by 12% in garment leathers.

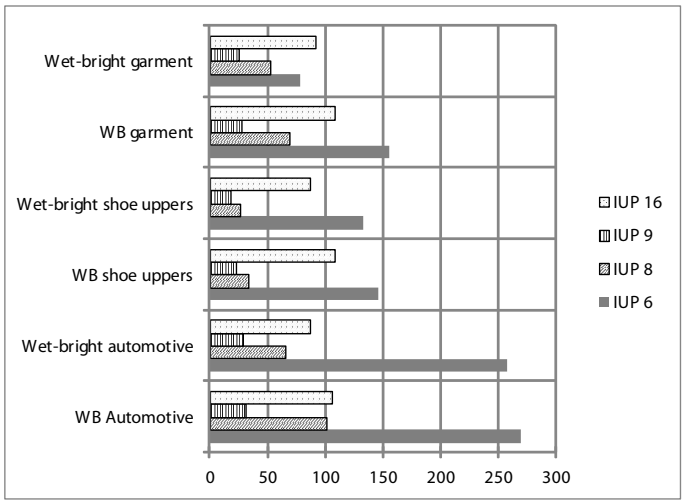

Figure 3. Physical tests after post-tanning processes.

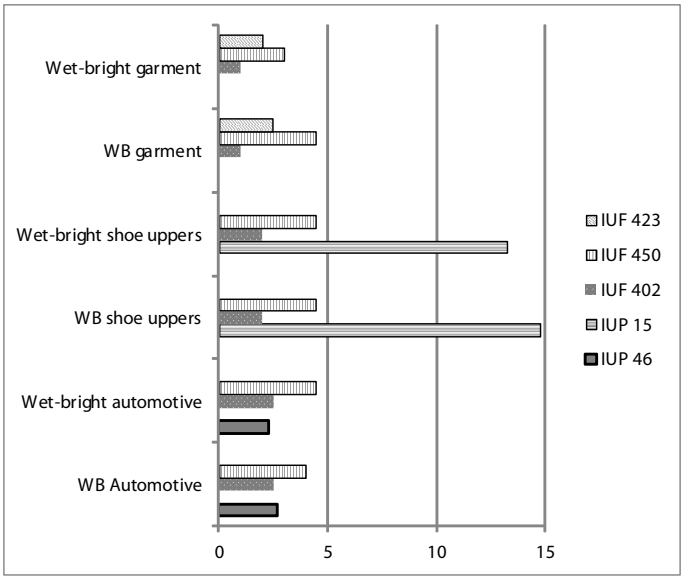

Figure 4. Physical tests after post-tanning processes.

TABLE VII
Comparison of pollution in wastewaters in post-tanning processes for each article.

TEST	WB Automotive	Wet-bright Automotive	WB Shoes	Wet-bright Shoes	WB Garment	Wet-bright Garment
Conductivity (μS /cm)	15183	17667	17970	20150	19400	20640
Suspended solids (mg/L)	3371	2291	761	356	976	648
COD (mg/L)	15450	9150	12100	10000	9500	8800
N – Kjeldahl (mg/L)	320	220	640	520	250	220
Chromium (mg/L)	102.5	No detectable	154.9	No detectable	203.9	42.5

And most important, wastewaters from the wet-bright leathers did not contain chromium. The chromium detected in wet-bright garment was due to the content of chromium salts in the post-tanning process. If this product were replaced by acrylic resins and syntans, the chromium in wastewater would not be detectable.

CONCLUSIONS

The new tanning process based on the aluminum-silicon compounds of Tanfor T™ produced perfectly white leathers meeting all of the requirements for automotive upholstery. The whiteness and strong cationic character of the intermediate substrate allowed for very bright colors. The leathers obtained with this process were free of chromium, aldehyde precursors and organic solvents. Only minor adjustments in retanning and fatliquoring were required compared to wet-blue. We believe that wet-bright qualifies as a universal tanning system because it produced leather meeting all of the current requirements for shoes, automotive and garments. Moreover, wet-bright leather did not contain chromium or heavy metals, and thus complies with Directive 2000/53/EC on End-of Life Vehicles. The new Tanfor T™ tanning system is environmentally friendly because it reduced COD by 60%, reduced, suspended solids by 61%, and reduced nitrogen by 65% compared with chromium tanning processes. Also important were reductions in COD, in suspended solids and in nitrogen after post tanning operations by using the wet-bright process compared with chrome tanning. And most important, wastewater from this new system contained no chromium.

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The Role of Neutral Salt for the Hydrolysis and Hierarchical Structure of Hide Fiber in Pickling

by

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Abstract

Pickling process carried out for adjusting the skin to the desired pH for tanning, in which neutral salts were added to avoid skin fiber from the acid swelling. This research study aimed at investigating the contribution of neutral salt to the hydrolysis and the fibrous structure of collagen fiber in acid solutions. Collagen fiber and bovine hide in sulfuric acid solutions with sodium chloride or sodium sulfate were investigated. The total protein concentration in the solutions was determined. The hierarchical structures of bovine hide in different acid and neutral salt systems were investigated by optical microscope, TEM and SEM. This study suggested the importance of neutral salt for the hydrolysis and the dispersion of collagen fiber in pickling. It implied that the osmotic swelling by acid could not reach the inner scale of fibril. The decrease in mechanical properties for the leather tanned with salt free pickling may have been caused by osmotic swelling destroying the interactions among the fibril and fiber bundles

Introduction

The most abundant protein of hide and skin is type I collagen, a fibrous protein, which is featured by its triple-helical conformation, formed by three left-handed polyproline II like helices twisted in a right handed triple helix with a length of about 300nm.[1-3] The hierarchical structures of hide and skin from molecular level to visible scale are consisting of collagen molecules, fibril, fiber and fiber bundle networks.[4-5] The collagen molecules, having lengths of 300nm with approximately 1.5nm in diameter, are self-assembled by a parallel staggering to form fibrils. The fibrils then regularly arrayed to form fiber bundles by a matrix rich in proteoglycans into fiber and fiber bundles, and the fiber bundles then weaved into network in three dimensions to form the corium layer of hide and skin. To obtain a good quality of leather, the fiber bundles of hide and skin should be dispersed or opened up adequately in beamhouse.[6-9] For example, to open up the fiber bundles, lime was used in the liming process, and enzymes were used in the bating process.

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Manuscript received November 6, 2013, accepted for publication January 30, 2014.

Pickling, a process immediately before chromium tanning in leather making, is to treat the hide and skin with acid and neutral salt solutions.[6] The main purpose of pickling is to adjust the collagen fiber of hide and skin to the desired pH for tanning. Furthermore, acid has the purpose to disperse the collagen fiber bundles and to impart the finished leather with good quality as well. The hide and skin will be swollen in acidic solutions due to the osmotic pressure. Adequate amount of neutral salt such as sodium chloride was added in the acid solution to avoid the swelling. The concentration usually is 5% of sodium chloride based on the water in the solution. It was reported that pickling process contributes to about 35% total dissolved solids (TDS) in the effluents.[10] To overcome the environmental problems of TDS related to neutral salts in the effluent, several of the novel processes have been developed.[11-13] Salt free pickling using naphthalene sulfonic acid is well known and extensively studied.[11] Oxazolidine based materials have been developed to displace neutral salt for salt-free picking process.[12] Recycle/reuse of pickle liquor for the subsequent batches as well as resorting to pickle free alum-chrome combination tanning systems have been studied.[13] However, the effect of neutral salts to the skin collagen fiber structure and the hydrolysis of collagen in pickling were seldom reported. In this paper, bovine hide was treated with various concentrations of acid and neutral salt solution, in which the hydrolysis of collagen fiber was analyzed and the hierarchical structures of collagen fiber were investigated by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and optical microscopy to illustrate the role of neutral salt for collagen fiber in acid solutions.

Experimental Procedures

Materials

The bovine hide used for this experiment was from Sichuan, China. The preparation of acid relaxed collagen fiber was described elsewhere.[14] Sulfuric acid, sodium sulfate and sodium chloride used in this experiment were chemical pure reagents. Chrome tanning agent is KMC-2 (Tingjiang Co. China), a self-basified chrome powder with 23% chrome oxide (Cr_2O_3) content and 33% basicity.

Treatments of Cattle Hide in Acid and Salt Solutions

The fleshed and unhaired bovine hide was cut into 20 × 20cm size. The cut was soaked in 0.1mol/L H_2SO_4 solution with various concentration of neutral salt with continuous shaking at 25°C. The 0.1% bromocresol green solution was used to determine the penetration of the acid, after the acid was penetrated thoroughly into the hide, stop shaking and over night. The swelling rate of the samples was determined according to the accumulation of its thickness as well as its weight. After 24h, a small piece was taken out and fixed with 4% formaldehyde (pH 7.4) for TEM and histological section investigations. The remaining part of the sample was tanned by 6% KMC-2 chromium tanning agent. The mechanical properties of tanned sample were determined by GT-AI-7000S Universal tensile testing machine (Gotech, China). All the experiments were done at least twice.

Treatments of Acid Relaxed Collagen Fiber in Acid and Salt Solutions

50mg freeze-dried collagen fiber was soaked in 100mL acid and salt solution of set concentration with continuous shaking for the set length of time. The concentration of sulfuric acid is from 0.1 to 0.5 Mol/L, in which the concentration of neutral salt is 0, 0.05, 0.1, 0.5 and 1.0 Mol/L respectively. The concentration of the hydrolyzed protein in the solution during the process was determined by Lowry method [15]. After treatment, the unsolved samples were fixed with 4% formaldehyde (pH 7.4) for SEM and TEM investigations.

Histological Investigation

The samples fixed in 4% formaldehyde (pH 7.4) over 24h were cut into 20um thickness sections by a freeze microtome (Leica, Germany). The cut section slides were stained with picric acid and fuchsin acid, with which the collagen fiber was stained into red. The stained sections were observed by optical microscope and recorded by a digital camera (Olympus, Japan).

Scanning Electron Microscopy (SEM) of Un-hydrolyzed Collagen Fiber

Samples of collagen fiber were attached to alum SEM stubs using carbon tabs. Specimens were sputter coated with gold prior to examination using a JSM-5900LV SEM (Japan Electron Optical Laboratory Co., LTD, Japan).

TEM Investigation

The unsolved collagen fiber was fixed in 4% formaldehyde solution and post-fixed in 1% Osmium tetroxide solution. After that the samples were gradient dehydration with acetone and embedded in epoxy resin. The Ultra-thin sections stained with uranyl acetate and lead citrate were observed with Hitachi H600-IV electron microscope at 75 kV (Hitachi, Japan).

Results and Discussion

The Effect of Neutral Salts to Collagen Hydrolysis in Acid-neutral Salt Systems

The commonly using neutral salt in leather making, sodium chloride and sodium sulfate were applied for this experiment. The sulfuric acid solutions were adjusted by various concentration of salt to create acid and neutral salt solutions, in which the collagen fiber was treated to a set length of time. The concentration of protein hydrolyzed into the solution was determined by Lowry method. The OD value is positive related to the concentration of the protein in solution.

The Concentration and the Type of Neutral Salt

The concentration of the neutral salt in 0.1 Mol/L H_2SO_4 solutions was set at 0, 0.05, 0.1, 0.5 and 1.0 Mol/L respectively. The hydrolysis profiles of collagen fiber in these solutions were shown in Figure 1. Sodium chloride and sodium sulfate showed different features to the hydrolysis of collagen in acid and neutral salt solutions. For sodium sulfate, 0.1 Mol/L of which in H_2SO_4 solution would reduce the hydrolysis rate of collagen fiber, while the hydrolysis rate would be depressed much more when the concentration of sodium sulfate in the solution increased to 1.0 Mol/L. For sodium chloride, when the concentration was 0.1 Mol/L in the solution, it would improve the hydrolysis rate of collagen fiber. However, when its concentration was 1.0 Mol/L in the solution, the hydrolysis rate would be depressed. These results could be interpreted by the salting in and salting out principles [16-18]. Sodium chloride showed salting in effect at low concentration while would show salting out effect at high concentration. Sodium sulfate showed better salting out effect than sodium chloride. The excellent dehydration effect of sodium sulfate plays a critical role in reducing the hydrolysis rate of collagen fiber in acid solution.

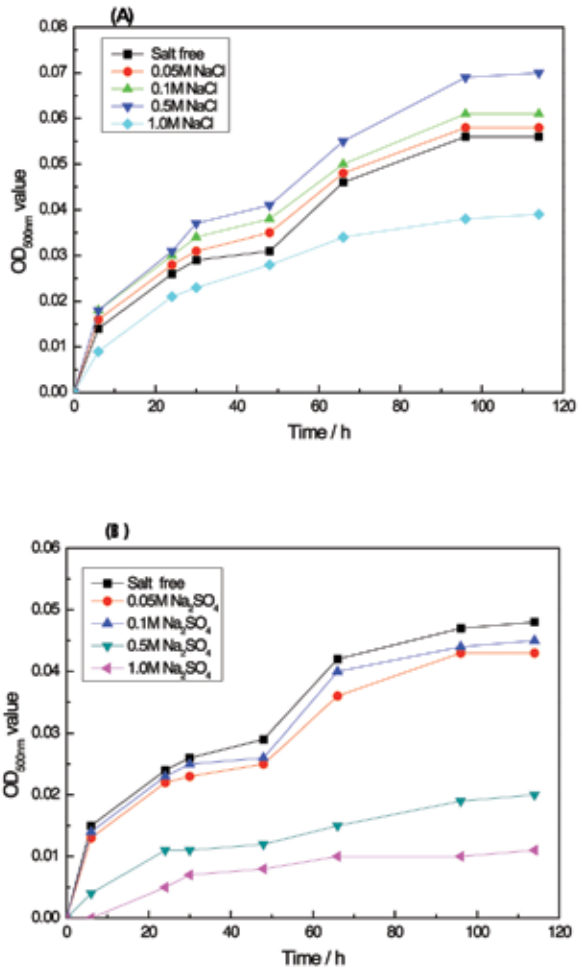

Figure 1. The hydrolysis profiles of collagen fiber in 0.1M H_2SO_4 & neutral salt systems at 25°C(A) 0.1MoL/L H_2SO_4 + NaCl; (B) 0.1MoL/L H_2SO_4 + Na_2SO_4.

The Concentration of Sulfuric Acid

The influence of neutral salt to the hydrolysis of collagen fiber in different concentration of H_2SO_4 from 0.1 Mol/L to 0.5 Mol/L was investigated. The hydrolysis profiles of collagen fiber in these solutions at 30°C were shown in Figure 2. The results showed that the hydrolysis rate of the collagen fiber would be increased according to the concentration of acid increasing. For different concentration of H_2SO_4, the low concentration of sodium chloride still showed salting in effect and the higher concentration of sodium chloride showed salting out effect. 0.5 Mol/L of sodium chloride showed salting in effect for 0.1 Mol/L of H_2SO_4, while would show salting out effect for 0.5 Mol/L of H_2SO_4. Sodium sulfate showed salting out effect for all the concentration acid as well (data were not shown).

Temperature

The influence of neutral salt to hydrolysis rate of collagen fiber in acid solutions at different temperatures was shown in Figure 3. It was shown that the higher the temperature was, the quicker the hydrolysis rate would be. When the treatment was set at 25°C, the hydrolysis of the collagen was much less than at 30°C or 35°C for the same treating period. More collagen would be hydrolyzed into the acid solution at higher temperature even the concentrated neutral salt was added. When the treatment of collagen fiber was above 30°C, the collagen will be dramatically hydrolyzed into the solution, suggesting a role of temperature for the hydrolysis of collagen in pickling and for the quality of the finished leather.

The Effect of Neutral Salts to the Hierarchy Structure of Hide Fiber in Acid and Neutral Salt Solutions

The bovine hide treated in 0.1 Mol/L H_2SO_4 solution with salt free was tanned by chrome tanning agent KMC-2. Its mechanical properties were compared with the chrome tanned leather by typical pickling. We noted that much longer time was needed for the chrome to penetrate thoroughly into the hide for salt free pickling. The content of Cr_2O_3 for leather treated by salt free pickling was 5.72%, which is higher than the typical pickling leather of 4.95% (Table I). It indicated that the swelling facilitated more of the chrome tanning agent to penetrate into the hide, although the swelling osmotic pressure hindered the penetration rate. The shrinkage temperature (Ts) could reach approximately 95°C for all the leather samples. It revealed that the leathers were tanned well enough by the two pickling methods. The tensile strength and tear resistance for salt free method's leather had the values of 8.38MPa and11.73N/mm respectively which were much less than the values of the leather by typical pickling (15.64MPa and 24.12N/mm) (Table I). These results suggest that the collagen fiber networks should be partly destroyed when the hide was existed in the swelling state.

The bovine hide treated within 0.1Mol/L H_2SO_4 at 25°C without salt would be swelled to semi-translucent with absorbing water. When the salt concentration was gradually

increased to 1.0 Mol/L, the hide would be dehydration to non-swell state. The bovine hide treated in 0.1Mol/L H_2SO_4 solution with salt free for 48h (Fig. 4A), and its optical microscopy photos showed that collagen fiber in the papillary layer and the reticular layer become larger and bigger because of acid swelling. The fiber bundles were separated and accompanied with collagen hydrolysis. When the neutral salt was added into the acid solution, with increasing salt concentration, the diameter of the collagen fiber became smaller and the distance among the fiber bundles also became closer (Fig. 4B, 4C). Fibers in the papillary layer showed compactly appearance, while the concentration of the salt raise up to 1.0 Mol/L, the linkage region between the papillary and the reticular layer were compacted adjacently, which means that the swelling of the hide was reduced completely. With the same concentration of neutral salt, the higher concentration of the acid was, the better separation of collagen fiber would be.

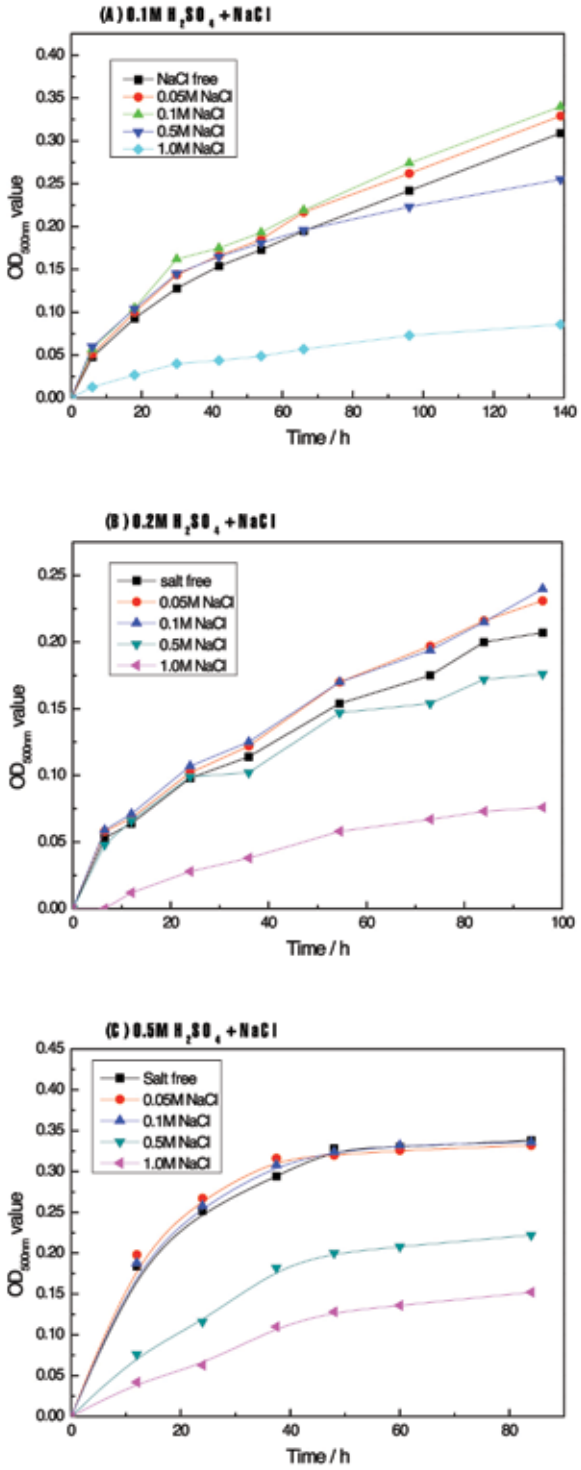

Figure 2. Hydrolysis profiles of collagen fiber in different concentration of H_2SO_4 and sodium chloride solutions at 30°C. (A): 0.1 Mol/L H_2SO_4 & NaCl; (B): 0.2 Mol/L H_2SO_4 & NaCl; (C): 0.5 Mol/L H_2SO_4 & NaCl.

The acid relaxed collagen fiber was treated with 0.1Mol/L H_2SO_4 solutions, the unsolved fibers were observed by SEM and TEM (Fig. 5). The SEM photos showed that the unsolved collagen fiber still maintained the fibrous structure perfectly, with evenly fiber diameter and smoothly surface, which was different to collagen fiber in alkali solutions [19]. The lower magnify pictures showed that the morphology of the fiber in acid solution with salt free has a large swelling tendency, and

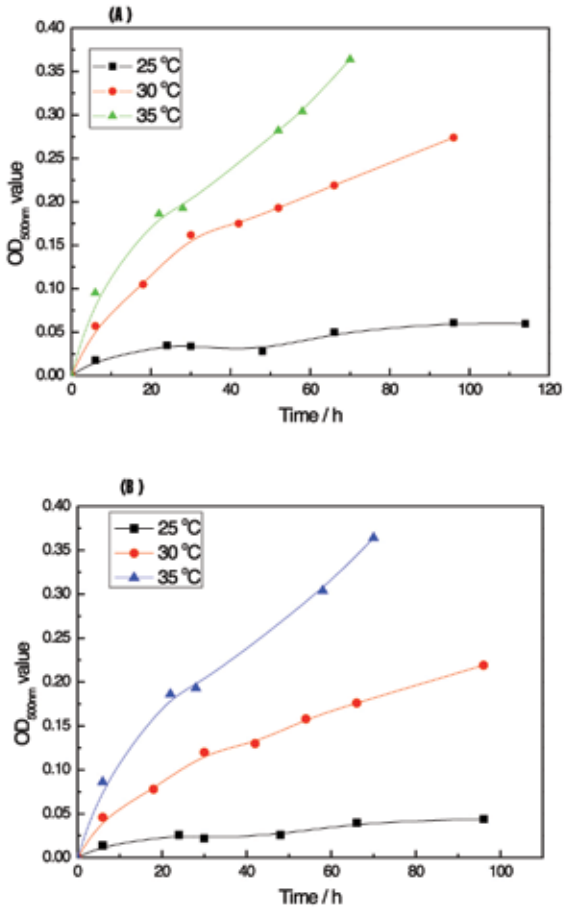

Figure 3. Hydrolysis profiles of collagen fiber in H_2SO_4 & neutral salt solutions at different temperatures. (A) 0.1Mol/L H_2SO_4 - 0.1Mol/L NaCl; (B) 0.1Mol/L H_2SO_4-0.1Mol/L Na_2SO_4.

the fiber was deformed and bended, suggesting the inner stress of osmotic pressure. This kind of deformation may influence the mechanical properties of the finished leather. The fiber treated with typical pickling process showed that the morphology of the fibers was not deformed and thus no inner stress existed. In turn, the swelling reduce was in consistence to the mechanical properties of the leather. The TEM graph of the unsolved fiber in 0.1 Mol/L H_2SO_4 showed clearly typical collagen pattern D-periodic bands, and the diameter of the fibril was the same as the original collagen fibrils. These results indicated that the swelling of the hide in acidic solution would not affect the scales inside the fibril. The fibril structure of hide collagen was packed by paralleling 1/4 staggered to a dense crystal structure, water molecules may be difficult to penetrate inside it.

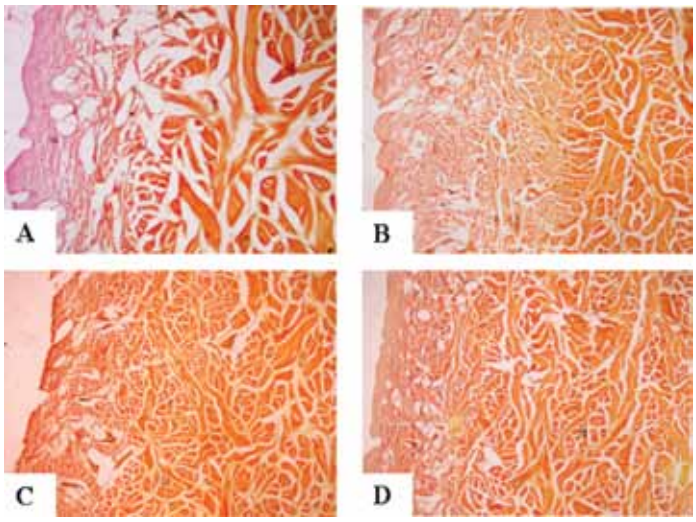

Figure 4. Histological graphs of cattle hide pickled in different salt concentration. The bovine hide was treated in 0.1mol/L H_2SO_4 with various concentration of NaCl at 25°C for 10h, after that, the samples were fixed with 4% formaldehyde for histological investigations. A: 0.0mol/L NaCl; B: 0.1mol/L NaCl; C: 0.5Mol/L; D: 1.0mol/L NaCl.

The hierarchical structures of the tanned samples were investigated by optical microscope and TEM (Fig. 6). The graphs showed that both kinds of pickling method have different morphology pattern. The fiber bundles of the sample for pickling with salt free were separated dramatically. The distance between the fibrils was dispersed widely, and the fibrils were distorted along the axial direction. Furthermore, it should be noted that the diameter of the fibril was unchanged, which implied that the swelling was only occurred at the fiber bundle and the fibril scales. For typical pickling process, the fiber bundles were arranged strictly, the distance of the fibrils showed no obvious change. These results also suggested the reason why the mechanical properties of the leather pickled with salt free were worse than the leather by typical pickling.

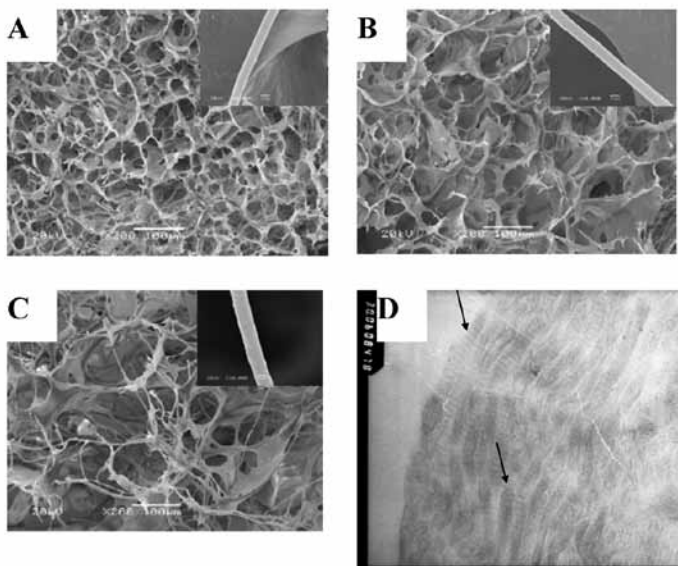

Figure 5. SEM & TEM pictures of collagen fiber treated in H_2SO_4 solutions with various Conc. of NaCl. The acid relaxed collagen fiber was treated in 0.1mol/L H_2SO_4 solutions with various concentration of NaCl at 25°C for 10h, the unsolved collagen fiber was freeze dried, then investigated by SEM(A, B, C) and TEM (D).,A: 0 Mol/L NaCl; B: 0.1 Mol/L NaCl; C: 1.0 Mol/L NaCl; D: 0Mol/L NaCl.

TABLE I

Properties of leather samples pickled in different salt concentrations.

Salt Conc. (mol/L)	Ts (°C)	Tensile strength (MPa)	Tear strength (N/mm)	Elongation at break (%)	Thickness swelling/%	Weight swelling /%	Cr_2O_3 (%)
0	94.6	8.38	11.73	70.19	80.4	44.0	5.47
1.0	95.2	15.64	24.12	81.85	13.7	0.0	4.95

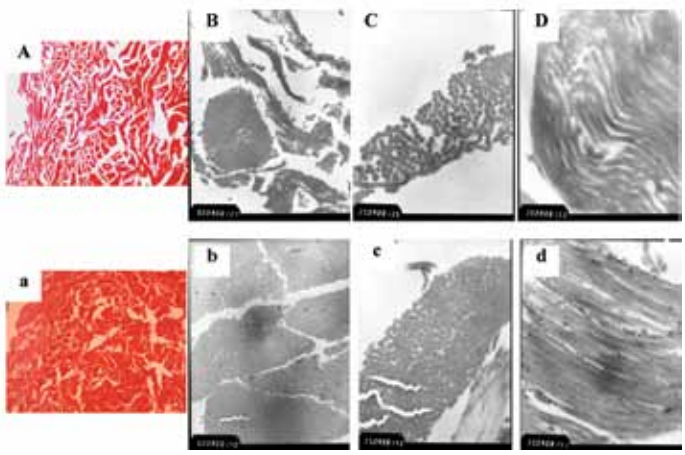

Figure 6. The optical microscope and TEM investigations of bovine hide pickled with typical pickling process (a, b, c, d) and without salt (A, B, C, D).

Conclusions

We examined the type and the concentration of neutral salt, the concentration of sulfuric acid and the temperature to the hydrolysis of collagen fiber in acid and neutral salt solutions. Sodium sulfate showed better inhibiting hydrolysis effect to collagen fiber than sodium chloride. More collagen would be hydrolyzed into the acid solution at the higher temperature even the concentrated neutral salt was added. The structures at the fiber scale were separated dramatically in acid solutions with salt free or with low concentration of salt since the osmotic stress among the collagen fiber was significant. While the concentration of sodium chloride was at 1.0 Mol/L, the fiber bundles would be packed closely and the swelling would be totally reduced. The results implied that the osmotic swelling by acid could not reach the inner scale of fibril. The mechanical properties were decreased for the tanned leather with salt free pickling, probably caused by osmotic swelling which destroyed the interactions among the fibril and fiber bundles.

Acknowledgement

The authors thank to the financial support of National High Technology Research and Development Program of China (No. 2013AA06A306) and RSF for ROCS (No.2012940-15-2).

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Life Lines

R. Aravindhan, see *JALCA* **101**, 445, 2006

K. J. Sreeram, see *JALCA* **106**, 239, 2011

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

Monica Puccini graduated in Chemical Engineering at the University of Pisa (Italy) in 2005. In 2009 she received the Ph.D. degree in Chemical and Materials Engineering at the Department of Chemical Engineering, Industrial Chemistry and Materials Science. She joined the research staff of the same Department as Assistant Professor in 2011 in the Industrial Chemistry and Technology sector. Her research is performed in the field of the industrial chemistry and it is focused on the modeling and environmental sustainability of chemical processes, on the research and development of thermo-chemical processes for energy valorisation of biomasses and industrial wastes, in the research and development of innovative processes in the leather industries and on the recovery and valorisation of industrial wastes.

Maurizia Seggiani graduated in Chemical Engineering at the University of Pisa (Italy) in 1993. She got her Ph.D. degree at the Department of Chemical Engineering, Industrial Chemistry and Materials Science in 1999. After an experience in ENEL Research Centre in Pisa, she joined the research staff of the same Department as Assistant Professor in 2001 in the Industrial Chemistry and Technology sector. Her research activities are focused on waste management, recycling and re-use of residues from coal and heavy-oil combustion, renewable energy resources, biomass and modelling of chemical processes.

Domenico Castiello graduated in Organic Chemistry rom the University of Napoli (Italy) in 1979. His experience includes ten years of tanning industry management. Since 2002 he has been the Director of PO.TE.CO. (Polo Tecnologico Conciario); the Tanning Technology Center of the Tuscany tanning industrial district. He follows research and development of innovative tanning processes and he is a teacher of professional and university courses.

Sandra Vitolo graduated in Chemical Engineering at the University of Pisa (Italy) in 1989. After experience in the process industry, she entered the Department of Chemical Engineering, Industrial Chemistry and Materials Science of the University of Pisa as Assistant Professor in 1992 in the Industrial Chemistry and Technology sector; Associate Professor from September 2000, she is Full Professor since December 2004. Her research interests include innovative and sustainable chemical processes and technologies; treatment, recovery and valorisation of industrial wastes and effluents; renewable energy resources, biomass, and biofuels.

Anna Bacardit, see *JALCA* **101**, 284, 2006

S. van der Burgh, completed his post doctorate at Wageningen University and Research Center, The Netherlands, in 2005. His study was the interaction between natural polyelectrolytes and globular proteins. Earlier he completed his PhD in colloid science (2005) and M.Sc. in food science (1998) at Wageningen. He then held positions as laboratory manager, product and technical development management for textile related chemical industries, before joining Kemira Chemsolutions in 2005. Presently, he is the Global Senior Application Manager Leather Market.

J. Armengol, chemist, the Universitat de Barcelona, specialized in Chemical Engineering. More than 15 years experience in sales and technical support within the chemical industry (mining, paper, detergents, textile, leather) including technical sales and sales management for Kemira Oyj, Spain, from 1998 to 2006. Then held sales/commercial positions in the ChemSolutions (Kemira Oyj) branch department in Spain. Presently he serves the company as global key account manager and technical customer support for specialties (including leather manufacturing).

Luís Ollé, see *JALCA* **101**, 284, 2006

Cheng Haiming is an associate professor in the Biomass and Leather Engineering Department, Sichuan University, China. His research focuses on cleaner leather making technology and collagen chemistry.

Chen Min is an associate professor in the Biomass and Leather Engineering Department, Sichuan University, China. Her research focuses on the histology of hide and leather.

Li Zhiqiang is a professor in the Biomass and Leather Engineering Department, Sichuan University, China. His research focuses on the application of enzyme for leather making.

ALCA 110th Annual Convention
June 18-20, 2014
Gideon Putnam Resort, Saratoga Springs, NY

Welcome to an exciting venue of events that will be unfolding for us from June 18 to June 20, 2014. We will host the 110th Annual Convention at the beautiful Gideon Putnam Resort at Saratoga Spring, New York. It is a first class facility that you can learn more about by logging on to their website at **http://www.gideonputnam.com**.

Again this year will be an email around mid March containing all details about the convention. Also voting for our Slate of Candidates will be done via email in late April. The online convention registration form has been updated and is ready for use or you can print out a form and send it to us. Visit **www.leatherchemists.org/annual_convention.asp** to download the registration form. Continue checking this website for new information and announcements about the 110th Annual Convention.

The schedule this year is entirely new. Prior to the official opening of the convention, the annual golf tournament will be held Wednesday, June 18, at the Saratoga Spa Gold Course beginning at noon. Pre-registration for golfers is a must to facilitate the start of the tournament. Further information on the golf outing will be found under the golf tab under this section.

The official opening of the convention will begin with Registration on Wednesday, June 18, from 5 to 7 pm in the Lobby followed by a Cocktail Reception and Dinner on the Gideon Patio. It will be a great time to have conservations with old and new associates in the leather industry.

ALCA President Steve Lange will open the Technical Program at 8 am on Thursday, June 19. This year's technical program is being organized by Vice-President Sarah Drayna and will offer a wide array of leather technologies covering tanning to finishing to environmental issues can be viewed in the coming months under this section of our website under Technical Program. The John Arthur Wilson Lecture will feature Jakov Buljan of Croatia. The title of his presentation is "Some Considerations about International Technical Cooperation in the Tanning Sector." The technical sessions will end at 4:45 pm followed by the Annual Fun Run at 5:30 pm. Thursday's activities will be capped off by a cocktail party at Portico from 7:15 to 8 pm followed by the Awards Banquet from 8 to 10 pm at the Arches. This will be an exciting evening that you won't want to miss.

Technical papers will resume Friday morning at 8 am with the Annual Business Meeting ending the morning sessions. At noon everyone is invited to attend the Sports Activities Awards Luncheon at the Arches from 12:15 to 1:15 pm. Prizes will be awarded for the Fun Run and golf outing as well as door prizes. The convention will close after the Sports Activities Awards Luncheon.

Please make plans now to join us for a wonderful time at the Gideon Putnam Resort.

Doug Morrison
Convention Chair

The 55th John Arthur Wilson Memorial Lecture

by
Jakov Buljan

Jakov Buljan will present the 55th John Arthur Wilson Memorial Lecture at our Annual Meeting, 8 am on Thursday, June 19, 2014. The title of his presentation is:

Some Considerations about International Technical Cooperation in the Tanning Sector

Mr. Buljan is the ex-Chief of the UNIDO Leather and Leather Products Unit, and presently a consultant. He has 48 years experience in the leather industry. His professional resume for his 48 years in he leather industry:

Current Contact Information:
Jakov Buljan
Mlinovi 62
10000 Zagreb, Croatia
Tel: **+385 1 4670107 ;**
Mobile: **+385 91 8966571**
E-mail: **jakov.buljan@zg.t-com.hr.** or **buljan.jakov@gmail.com**

Academic qualifications:

- B.Sc. in Biotechnology, University of Zagreb (1966), Croatia
- Languages: English, German, working knowledge of French, Spanish and
- Croatian (mother tongue)

Professional Experience:

- **1966-1974**
  Initially in charge of process and quality control, subsequently works manager at CIBALIA, Vinkovci, Croatia, one of the largest European skin tanneries, leading producer in goat suede and specialist in hair sheep nappa.
- **1974-1977**
  General manager of the newly founded BOKIYU Tanneries Ltd., a joint venture company in Madras (now Chennai), India, responsible for design, commissioning, start up and operations of the tanning plant. Involved in introducing production of finished leathers from E.I. (vegetable tanned skins) in several local tanneries.
- **1977-1981**
  Various senior managerial positions at the parent company CIBALIA, Vinkovci; direct involvement in optimizing daily operations & output, including product development. Subsequently responsible for overall raw material procurement and leather sales and appropriate company profile in fairs with frequent travels to China, India, Bangladesh, Sudan and Ethiopia.a A member of MODEUROPE for several years.

Jakov Buljan

- **1980**
  A six-month UNIDO consultancy assignment in Bujumbura, Burundi to assist the local tannery to start production of wet blue hides.
- **1981-1983**
  Tripoli, Libya based country representative of INGRA, a consortium for supply of industrial plants on a turnkey basis.
- **1983- 2003**
  Senior) Industrial Development Officer, Leather and Leather Products Unit, ultimately **Deputy to the Director**, Agro-industries and Sectoral Support Branch, United Nations Industrial Development Organization, (UNIDO) Vienna, Austria.
- **2003 – to date**
  Upon (mandatory) retirement from UNIDO active as a free-lance consultant. Carried out several field missions to Nigeria, India, Italy, China, Tunisia, Mexico, Bangladesh, and Ethiopia dealing with cleaner technologies, waste treatment, establishment of tannery industrial zones, competitiveness improvement etc.

Keynote lecture at XXXI Informations- und Diskussionstagung, Leather Institute and Tanning School Reutlingen, Germany in 2004. Lecture at UNIDO Leather and Leather Products Industry Panel, León, Mexico, (2005).

Papers, publication, lectures and field projects:
Technical editor, author and/or co-author of numerous technical papers, studies, brochures and video films. Completed thirteen reports and pilot projects for UNIDO and many wastewater treatment plant projects in India, China and Africa. [*Contact the JALCA editor for a specific detailed listing of publications papers and projects*.]

RFW2.14

American Leather Chemists Association
2014 Spring Meeting of the
Research Liaison Committee
USDA, ARS, Eastern Regional Research Center
Wyndmoor, Pa

Date: Tuesday April 22, 2014, 9:00 am to 4:30 pm

The purpose of the ALCA RLC is to maintain an awareness of ongoing hides and leather research, to foster research collaboration, and to assist the USDA and other public research institutions in establishing research priorities.

The Research Liaison Committee meets twice a year, once in April at the USDA Eastern Regional Research Center and then during the ALCA annual convention in June to review industry trends and requirements. The RLC polls members of the ALCA, the U.S. Hide, Skin and Leather Association (USHSLA) and members of the Leather Industries of American (LIA) to identify and prioritize the immediate and long-term needs of the industry for by-product hides.

Membership and attendance at the RLC Spring Meeting is open to those affiliated with leather manufacture. Those attending represent hide producers and dealers, tanners, production management, product development executives, researchers, scientists, consultants, chemical suppliers, industry & trade lobbyists, students and those connected to the study & usage of collagen.

Proposed topics include:

- Recap of the global and U.S. raw material market
- Update on issues pertaining to the U.S. hide & leather industry (USHSLA)
- A regulatory and trade update
- Recap of domestic leather activity
- Update on status of ERRC hides and leather program
- Reports from ERRC from hides and leather program covering such areas as pretanning, physical properties of leather, alternative tannages, byproduct utilization and finishing, leather quality and non-destructive testing.

For further information, contact Lori Hyllengren at (651) 258-4338 hyllengren@sbfoot.com or Ellie Brown at (215) 233-6481 ellie.brown@ars.usda.gov.

Scholarship Application Available

Randall L. Rowles

Applications for the Randall Rowles Memorial Scholarship are now available through the ALCA office by either writing to ALCA, 1314 50th Street, Suite 103, Lubbock, TX 79412; or by emailing to alca@leatherchemists.org; or by calling (806) 744-1798.

Guidelines for the scholarship include that the recipient of the scholarship shall be either a child or grandchild of an ALCA member in good standing and currently enrolled in school full-time, having completed at least two years of post-secondary education with a declared major in the sciences or leather-related field. A current college transcript must be submitted to the ALCA office along with an application.

The scholarship shall be based on merit. The GPA of the applicant will be a significant criterion for the selection committee.

Completed applications must be received at the ALCA office no later than May 1, 2014. The selection of the recipient will be made no later than June 1, 2014. Members of the Selection Committee will be Lori Hyllengren, Nick Latona, Steve Lange, Okey Abara, Kadir Dönmez, and Cheng-Kung Liu.

The amount of the scholarship is $500, and the recipient will be announced at the Annual Business Meeting of the Association on Friday, June 20, 2014, at Gideon Putnam Resort, Saratoga Springs, NY.

THE AMERICAN LEATHER CHEMISTS ASSOCIATION
1314 50th Street, Suite 103, Lubbock, Texas 79412-2940
Ph: 806-744-1798 **Fax**: 806-744-1785 **Web**: www.leatherchemists.org
Email: alca@leatherchemists.org

Obituary
Paul D. Finnegan

Paul D. Finnegan

Billerica, MA — Paul D. Finnegan, formerly of Lowell, died Wednesday, February 5, 2014, after a brief illness with his family by his side. He was the widower of the late Marilyn R. (Condon) Finnegan who died in 2004. A son of the late Cornelius T. and the late Mary E. Finnegan, he was born November 17, 1926, in Lowell, He attended Sacred Heart Grammar School, and graduated from Lowell High School. Paul served in the U.S. Coast Guard from 1944 to 1945. He attained a Bachelor's Degree in Leather Engineering from Lowell Technological Institute in 1959.

He was a firefighter for the City of Lowell Fire Department for over 10 years before working for the A.C. Lawrence Leather Company - first in Peabody, and then for over ten years as the Superintendent of the company's tannery in South Paris, Maine. He retired from A.C. Lawrence as Director of Environmental Affairs after over 25 years with the company.

He was a member of the American Leather Chemists Association, serving on many committees and Council. He was the recipient of the 1987 ALCA Fred O'Flaherty Service Award. Said award presenter Anton K. Mayer; "He is a man who has devoted nearly his entire career towards technical advances and innovations in the tanning process, but more specifically in the environmental area of leather making…. he organized and chaired very successful symposia, held at the ALCA annual meetings in 1978, 1979, 1980, 1981, 1982, 1986 and again in 1987, and was a former President of The New England Tanners Club."

He is survived by his daughter and son-in-law, Martha Ann Finnegan and Ernest V. Linek of North Billerica, his brother, Robert F. Finnegan and his wife, Rita, of Hampton, NH, his sister, Patricia A. Morais of Rye, NH, and many nieces and nephews. He was also a brother of the late Frederick J. Finnegan, the late Cornelius T. Finnegan Jr., the late Marie F. Lynch, and the late John T. Finnegan.

CA/RFW 3.9.14

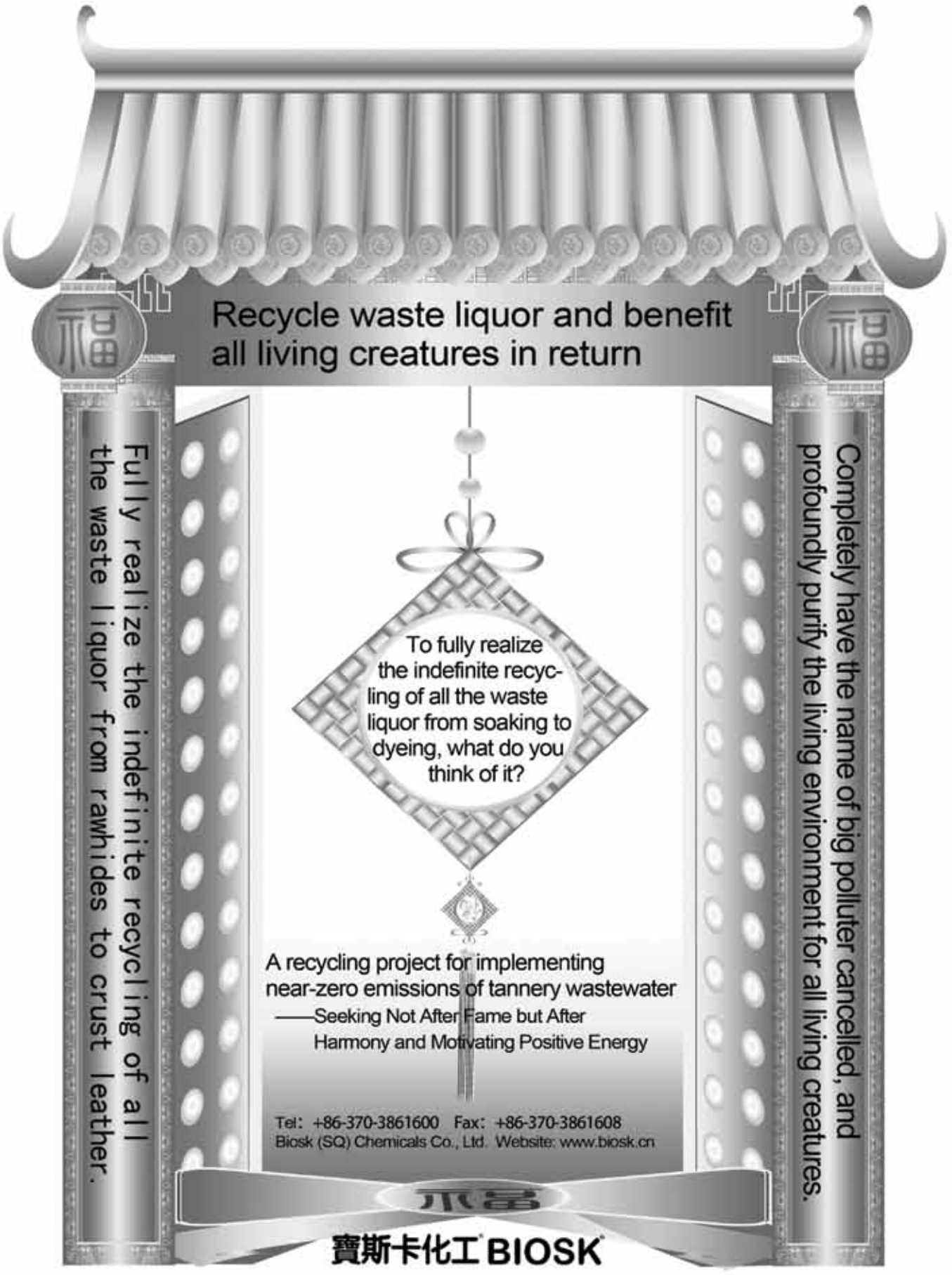
Obituary
Steven R. Miller

Longtime member and friend of the ALCA, Steven R. Miller, passed away February 2, 2014, in Brazil. Quoting from the annoucement made by his company, "With upmost grief, JBS informs that Steven Robert Miller passed away this morning. Steve was the Technical and Innovation Director of JBS Couros. He was a great professiona, a unique human being and a friend. The JBS family is mourning the death of a kind friend, who for more than 40 years was an example of professionalism and dedication contributing towards the development and growth of the global letaher industry and the implementation of best practices in this business. JBS wishes to extend sincere condolences to the Miller family and friend." We too extend our deepest sympathies to his entire family and friends.

Steven R. Miller

Steve Miller joined Robson-Lang Leathers Ltd in Cobourg, Ontario, Canada in December 1973, graduated from the National Leather Sellers College in June 1977 and relocated to the Robson-Lang tannery in Barrie, Ont, Canada. September 1981, he joined Garden State Tanning at Williamsport, MD as assistant Tanner. In 1983, he transferred to GST Reading, PA, eventually to the position of Production Tanner. October 1991 he joined Eagle Ottawa, Grand Haven, MI as the R&D Technical Manager. February 1992 he accepted the position of Technical Director for Eagle Tanning, Waterloo, IA. August 1998 he joined Seton Company as R&D Manager in Brandsen, Buenos Aires, Argentina. October 1999 he was promoted to the position of R&D Projects Manager, Seton Americas. In 2009 he moved to Brazil to work for BMZ Couros Montenegro as their technical coordinator for automotive leather development. From 2010 to 2011 he was the technical and commerical coordinator for automotive leather development for JBS Couros, then serving as Director of Technical and Quality for JBS world-wide from 2012 to the present.

He was a member of the ALCA from 1988 to 2010, served on the Education Committee from 2001 to 2009, and was a Councilor from June 2004 to June 2007. He also was a member of the Canadian Tanners Production Club's Education Committee, the Education Committee Chairman, the Secretary of the CTPC and finally Treasurer.


Recycle waste liquor and benefit all living creatures in return
Fully realize the indefinite recycling of all the waste liquor from rawhides to crust leather.
Completely have the name of big polluter cancelled, and profoundly purify the living environment for all living creatures.
To fully realize the indefinite recycling of all the waste liquor from soaking to dyeing, what do you think of it?
A recycling project for implementing near-zero emissions of tannery wastewater
——Seeking Not After Fame but After Harmony and Motivating Positive Energy
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寶斯卡化工 BIOSK

Few people realize that Leather Making is the world's oldest manufacturing process, thus the world's oldest industry. Tanning—the process of converting hides and skins into leather—is also the world's first science. Also, because of the pure craftsmanship involved, tanning may well be the world's first art form.

Anyone who doubts that a sheepskin has up to 30,000 fibers per square inch has only to count them.

NOTHING TAKES THE PLACE OF LEATHER

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- ✓Better Fungicidal Efficacy
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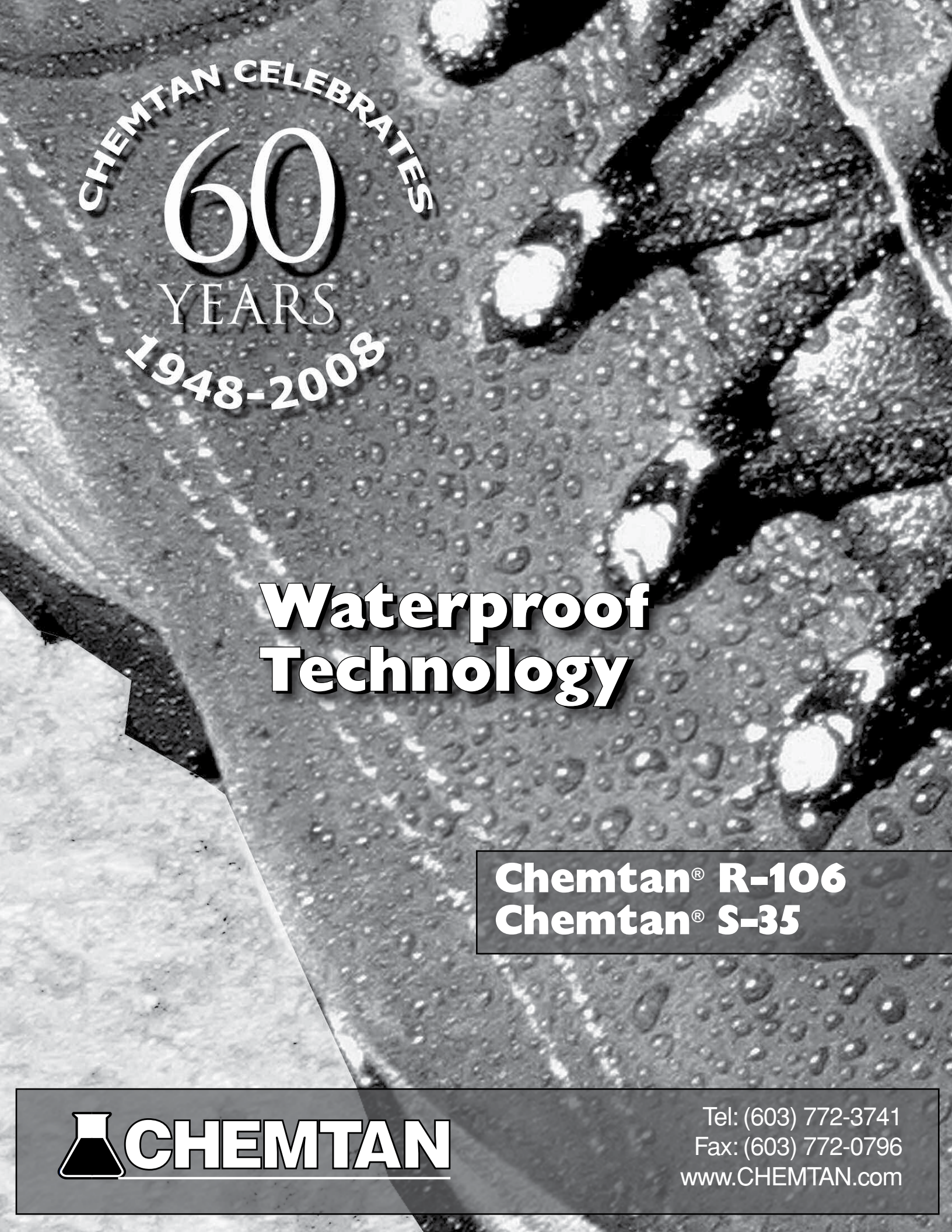

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