List of Oral Presentation

Session-Wise

Table of contents

S.No	Title of Paper	Corresponding Author	Page No
Session 1: Fundamentals in Leather Science			
1	Site-Specific Interaction of Polyphenols on Collagen Using Model Collagen Peptide	Madhan B	1
2	Measuring the heritability of traits in sheep and deerskin	Geoffrey Holmes	7
3	Chrome-tanned leather shrinkage probed with modulated temperature differential scanning calorimetry	Richard Leslie Edmonds	15
4	Influence of naphthalenesulfonic acid derivatives on the properties of the hide. Part II	Olga Ballús	21
5	Surface Area Gain Of Leathers Dried Under Different Conditions	Hüseyin Karavana	30
Session 2: Advances in Chemicals for Smart and Intelligent Leathers			
6	Waste to wealth approach Adhesive from the unused goat head skin	Md Abul Hashem	36
7	Fabrication of Antibacterial Casein-based ZnO Nanocomposite for Leather Finishes through In-situ Route	Wang Yanan	41
8	Ionic Liquids New age designer chemicals for leather processing	Nishad Fathima N	48
9	A New Age Chromium-Melamine Syntan Towards Quality Upgradation of Lower-end Raw Materials	Sathish Murali	58
10	Novel surfactants in Leather Processing	Vijayabaskar V	65
11	Tanning with a Gallic extract in combination with a cationic ester for the production of high performance leathers.	Eric Poles	70
Session 3: Innovation and Value Addition for Leather			
12	Intelligent real time leather defect detection system using image processing technique	Malathy J	81
13	Analysis of characteristic odor compounds in leather by GC-MS and GC-Olfactometry	Hirohiko Washiya	88

14	Method for determining the optimized exhaustion of fatliquors to minimize the ETP-inflow	Dirick von Behr	93
15	Artificially induced collagen fibril orientation affects tear propagation in leather	Susyn Kelly	103
16	Chrome-free Tannage Suede Garment Leathers from Rural Vegetable Sheep Crust Leathers	Ali Elnaeim Musa	113
17	Effect of binder selection on topcoat property retention after accelerated weathering	Joe Hoefler	122

Session 4: Strategies for Sustainability

18	Enzymatic unhairing permeability assay of bovine skin epidermis with enzyme extracts	Betina Galarza	133
19	Preparation and characteristics of surface modified PAN fiber by collagen	Ding Zhiwen	142
20	Study on the Recycling Technology of Unhairing-Liming and Tanning Wastewater	Jin Liqiang	151
21	Different pre-treatments of chrome tanned leather waste and their use in the biogas production	Carolina Scaraffuni Gomes	163
22	Sustainable Leather Management A mass balance bench mark of different chromium tanning technologies	Dietrich Tegtmeyer	175
23	Formaldehyde and Acetaldehyde in Leather: Similarities and Discrepancies	Jochen Ammenn	181
24	Redefining Chrome Tanning A Waterless Approach	Thanikaivelan P	185
25	Concept of Sustainability - Looking Forward	Anne Lama	192
26	The elimination of effluent from liming acid/salt pickling and chromium tanning verified by five years high-volume wet blue leather manufacture.	Richard Daniels	202
27	Probiotic solutions for sustainable leather	Juan Carlos Castell Escuer	209

Session 5: Emission control technologies

28	Clean salt recovery and water recycling using Nanofiltration and Reverse Osmosis	Wolfram Scholz	218
29	Biodecolorization and biodetoxification of leather dyes from aqueous solution and dye-containing effluents by native white-rot fungi strains	Santiago Ortiz Monsalve	223
30	Novel Formaldehyde Scavenger Containing Active Methylene for Efficient Removal of Formaldehyde in Leather	Zhang Ting	234

31	Analysis of flow and energy aspects of Zero Liquid Discharge (ZLD) technology in treatment of tannery effluents in Tamil Nadu India	Jakov Buljan	244
32	Studies on simultaneous removal of nitrogen and organic carbon from tannery wastewater using Airlift sequencing batch reactor	Aysanew Gorems Melesse	260
33	Microbial fuel cell a novel technology for effluent treatment and electrical energy generation	Divyalakshmi P	269
34	Technological developments for total dissolved solids (tds) management and environmental sustainability in asian leather sector	Rajamani S	277
Session 6: Design innovation for lifestyle leather products			
35	New Dimensions in Childrens Shoes	Md Sadiq	287
36	Dynamic Plantar Pressure Analysis of persons with Diabetis, An Approach to improve the design of Therapeutic Footwear	Sathish Babu G	292
37	Reduction of Skin Disorders by HCHO in Leather Products	Daisuke Murai	297
38	Comparision of visual asorting process and spectral photometer usage in leather apparel production	Mehmet Mete Mutlu	304
Session 7 & 8: Enriching human capacity/ Global research alliances and partnerships			
39	eLearning and Blended Training in the Leather Professional Education	Ivan Kral	313
40	Role of CSIR-CLRI in Skill India initiative enriching primary level human resource through artisanal skill development	Kanimozhi B	324
41	Indo-Ethiopian Alliance for Transformation of Ethiopian Leather Sector	Chandrasekaran B / Wondu Legesse	332
42	Development of an International Proficiency Testing by Interlaboratory Comparison Applied to Physical and Chemical Test Methods for Mineral Tanned Lea	Carlos Amador Meza Moya	337

FLS O-01

UNDERSTANDING THE INTERACTION OF COLLAGEN AND POLYPHENOLS: MOLECULAR INSIGHTS ON VEGETABLE TANNING

Balaraman Madhan*, R.Ravikanth Reddy, B. V. N. Phani Kumar, Ganesh Shanmugam,

NMR Lab, Inorganic & Physical Chemistry Department, Organic & Bioorganic Chemistry Laboratory,
CHORD, CSIR-Central Leather Research Institute, Adyar, Chennai-600 020, India.
Academy of Scientific and Innovative Research (AcSIR), Anusandhan Bhavan, 2 Rafi Marg,
New Delhi 110 001, India.

Tanning is a process by which collagen matrix is stabilized to prevent putrefaction against heat, enzymatic biodegradation, and thermo-mechanical stress. One of the tanning processes involves with vegetable tannage, which consists of polyphenols. Hence the interaction of polyphenols with collagen may provide valuable information to understand the tanning process involved leather processing. Although several reports have been published on the interaction of collagen and polyphenol interactions, the site-specific interaction of polyphenol with collagen is not completely understood. One of the possible reason could be the lack appreciate technique which explores the site-specific interactions of polyphenols. Although NMR is a powerful technique to extract atomic level interaction between protein-polyphenol interactions, it is not an appropriate tool to investigate collagen-polyphenol interaction due to high molecular weight of collagen which precludes the use of NMR. However, in this study we have investigated the site-specific interaction of polyphenols such as Gallic acid, Catechin, Epigallocatechin gallate and Tannic acid with model collagen peptide (MCP), which has a molecular weight range of 10 kD, using spectroscopic techniques mainly 2D HSQC. MCP mimics the triple helical nature of native collagen. The presentation will cover preferential binding sites/groups in MCP for polyphenols.

Keywords: Collagen, polyphenols, NMR spin relaxation, STD and Circular Dichroism.

INTRODUCTION

Though tanning, particularly vegetable tanning dating back to the history of mankind, a precise molecular insight on the same is still eluding. Understanding the molecular events implicated in the tanning of collagen has been a great interest for leather chemists. The structural basis of collagen, the leather making protein has been well investigated and understood. Out of XXIX types of collagen identified till date, Type I is the most abundant protein of the extracellular matrices including skin. Collagen comprises of three left-handed α-chains and are known to build up together a right-handed triple helix, which is stabilized through inter-chain hydrogen bonds. Ramachandran and Chandrasekaran suggested that collagen molecules are further stabilized by water-mediated hydrogen bond. Earlier work has also traced the mechanism of stabilization of collagen brought about by hydroxyproline through water-mediated hydrogen bonding. The hydrogen bonding interactions proposed by the Madras Group are well exhibited in the structure that directly linked by hydrogen bonds to the carbonyl oxygen atoms of Gly and the hydroxyl oxygen atoms of Hyp, as reported in the previous structures like (Gly-Pro-Hyp).

The effects of a wide variety of tanning agents on the measurable properties of collagen through a common (even semi-empirical) correlation. An attempt has been made in our group to relate shrinkage temperature changes with long-range order and stability gained by collagen against enzyme promoted hydrolysis with the inhibitory potentials of chromium and polyphenolic species on collagenase. The role of structure and dynamics of water around the protein sites in tanning has been believed to be important; Nuclear magnetic resonance (NMR) spectroscopic parameters most useful in the study of water are the relaxation times. Water molecules exchange rapidly between a free state, similar to that of neat lattice water and a bound state affected by the presence of proteins and macromolecules.

MATERIALS AND METHODS

Gallic acid, Pyrogallol, (+)-Catechin, (−)-Epigallocatechin gallate, Quercetin, Tannic acid, Deuterium oxide (D_2O) and 4, 4-Dimethyl-4-silapentane-1-sulfonic acid (DSS) were purchased from sigma Aldrich (Bangalore, India), Rat tail tendon collagen (type-I). Model Collagen Peptide mimicking the collagen triple helical structure and functional behavior was custom made from Tufts University.

Sample Preparation

The NMR samples were prepared in 90 % H_2O and 10 % D_2O in 50 mM CD_3COOD and the pH of the solution is 3.5-3.6.

NMR Spectroscopy

NMR experiments were performed on a Bruker Avance II HD Nano Bay 400 MHz for the characterisation of model collagen peptide (MCP), homonuclear experiments Such as Total correlation Spectroscopy (TOCSY), nuclear overhauser enhancement spectroscopy (NOESY) experiments are performed. NOESY spectra for MCP were obtained at mixing times of 350 ms with 64 scans. The 2D spectra were collected with 512 t1 increments and 1k data points in the t2 dimension. The spectral width is 10 ppm on both dimensions and 1 Hz line broadening was applied. Total correlation Spectroscopy (TOCSY) spectra for MCP were obtained at mixing times of 80 ms with 64 scans. The 2D spectra were collected with 512 t1 increments and 512 data points in the t2 dimension. The spectral width is 10 ppm on both dimensions and 1 Hz line broadening was applied. The ^1H detected heteronuclear multiple quantum coherence spectroscopy (HMQC), HMQC TOCSY. HMQC NOESY, HSQC TOCSY, HSQC and HSQC NOESY were collected with 128 t1 increments and 2k data points in the t2 dimension using the echo-Anti echo method. The 27-mer $(GXY)_9$ forms a trimer with a triple-helical conformation in aqueous solution and undergoes a thermal transition to a monomer at 60ºC.

Assignments of MCP

The ^{15}N heteronuclear Single quantum coherence spectroscopy (HSQC) shows signals for the four labeled residues in the spectra. The HSQC spectrum of the MCP in 90% H_2O 10% D_2O at 25ºC where the peptide is shows mixture of monomer and trimer peaks. The $(GXY)_9$ sequence contains 6 proline, 6 Hydroxyproline, and 9 glycines are present in each chain. Due to the extensive overlapping of the resonance, we are not able to see all residues in each chain. Even though we identified using TOCSY, NOESY, HSQC, HSQC TOCSY and HSQC NOESY. To observe trimer formation and the overlapped signals we performed the experiments at different temperature at 5º C 25ºC and 55ºC. Each glycine has additional peaks indicates signals from both monomer and trimers.through TOCSY, we identified the amino acids and adjacent 15N labeled Glycines.

Adjacent amino acids sequence connectivity obtained from the NOESY spectrum. Sequential connectivity was observed between Proline, Hydroxyproline, and Glycine1 through NOESY spectrum Sequential connectivity is observed between leucine and Glycine 3 which is further confirmed by connectivity are observed between Alanine and glycine 3 through NOESY spectrum.

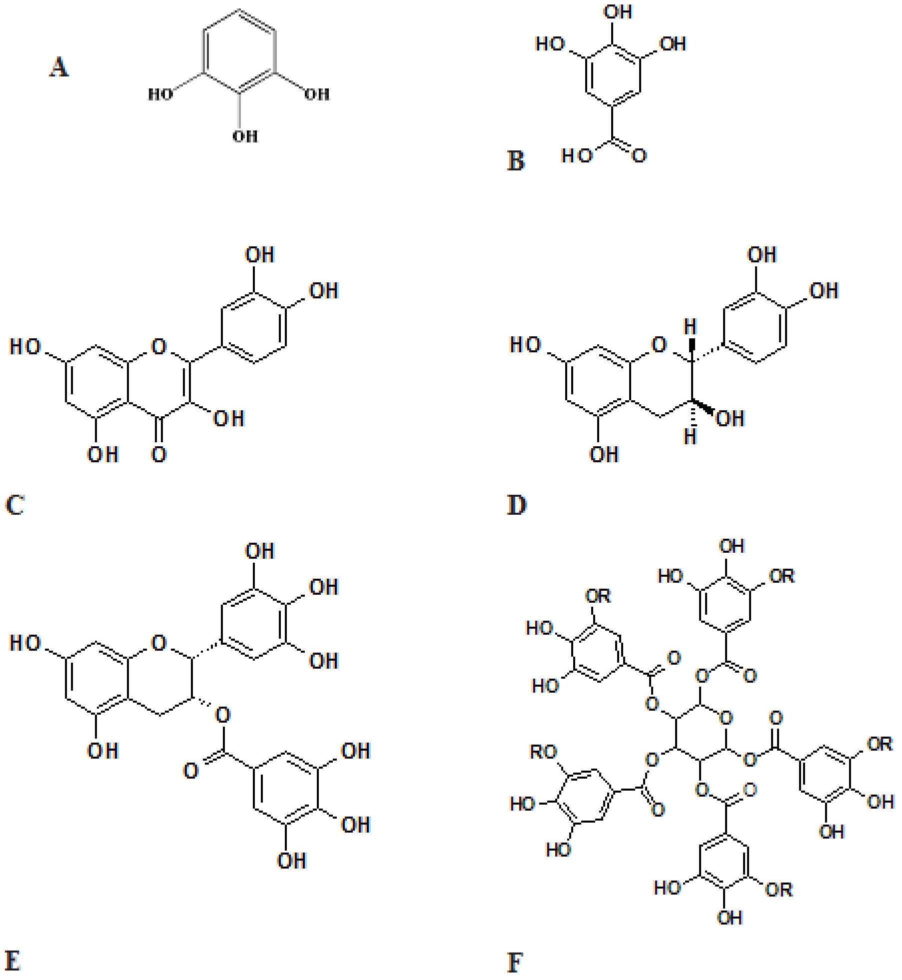


Figure 1 Plant polyphenols used for understanding collagen-polyphenol interactions A) Pyrogallol (PG) B) Gallic acid (GA); C) Quercetin (Quer); D) Catechin (CA), E) Epigallocatechin gallate (EGCG) and F) Tannic acid (TA).

RESULTS AND DISCUSSION

The dynamics of water can be related to structural alterations in collagen and with the presence of polyphenols had been studied. ^{1}H longitudinal relaxation time (T_1) and transverse relaxation time (T_2) decay profiles of native and polyphenol viz., GA, Quer, and CA were studied earlier[9]. We found all the three polyphenolic molecules to affect the water structure around collagen, and Catechin affected the water structure the most out of the three polyphenols studied, and the effect was correlated with the shrinkage temperature rise, where it was seen that Catechin exhibits higher shrinkage temperature than the other two polyphenols studied.

Recently, we have used saturation transfer difference (STD) NMR for probing collagen-polyphenols interactions. STD exploits the protein magnetization as a reservoir and upon saturation, the protein magnetization suffers from spin-diffusion / cross relaxation / magnetization exchange leading to effective saturation of protein. Hence, the ligands which are in the close proximity of protein binding will encounter major intensity enhancements due to the saturation transfer from protein to ligand and subsequently provides fruitful information on ligand epitope-mapping. The molecular level interaction between collagen and various small molecules such as a Gallic acid (GA), Pyrogallol (PG), Catechin (CA) and Epigallocatechin gallate (EGCG) were studied with the aid of NMR measurements like ^{1}H spin-relaxation times (T_1 and T_2) and saturation transfer difference (STD) NMR. The ^{1}H spin-relaxation and ^{13}C chemical shift data analysis reveal that –COOH group of GA preferentially binds to collagen while PG does not show any significant binding affinity to collagen. STD NMR data indicates that the resonances of H-6, H-8, H-2′, H-5′ and H-6′ protons of CA and H-6, H-8, H-2′, H-6′, H-2′′ and H6′′ protons of EGCG persist in the spectra, demonstrating that these protons are in spatial proximity to collagen which is well corroborated with 1H spin-relaxation analysis. The current NMR results thus provide an evidence for the binding of GA, CA, and EGCG to collagen at a molecular level.

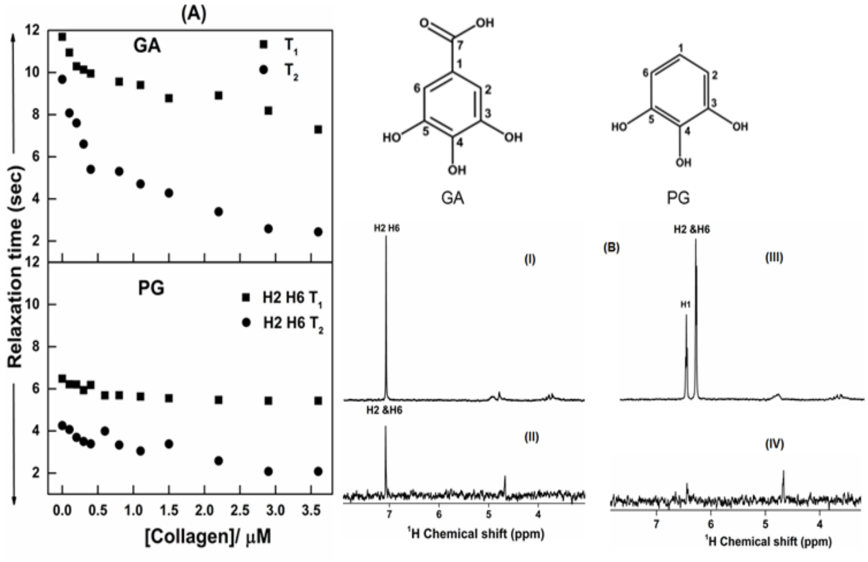


Figure 2 (A) T_1 and T_2 relaxation times of the protons in GA (6 mM) and PG (6 mM) in the presence of different concentrations of collagen. (B) ^{1}H NMR spectrum of GA (6 mM) in the presence of collagen (6 µM) and the corresponding STD NMR spectrum are shown in (I) and (II), respectively. Similarly, spectra for PG (6 mM) at the same collagen concentration are displayed in (III) and (IV), respectively.

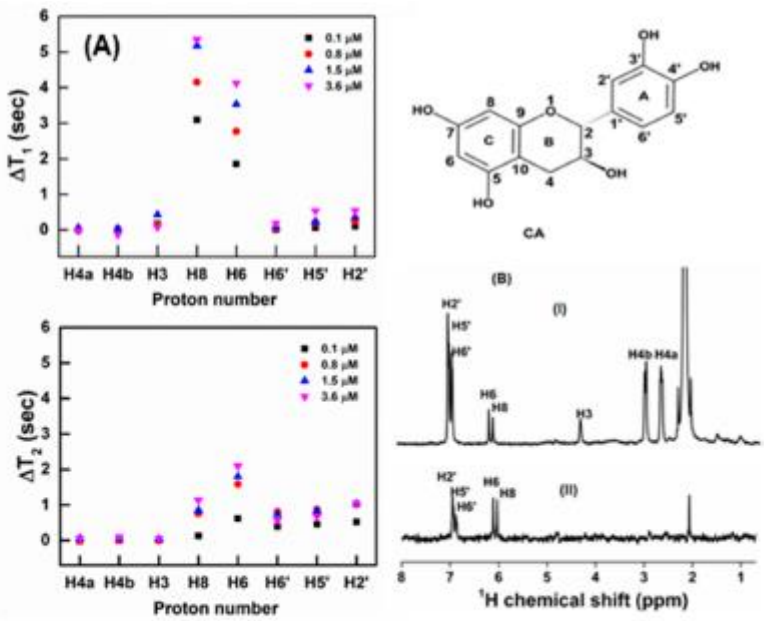


Figure 3 (A) ^{1}H T_1 and T_2 relaxation times of CA in the presence of different concentrations of collagen relative to CA (6 mM) alone. (B) 1D proton NMR of CA (6 mM) in the presence of collagen (6 μM) is shown in (I), while corresponding STD spectrum is displayed in (II).

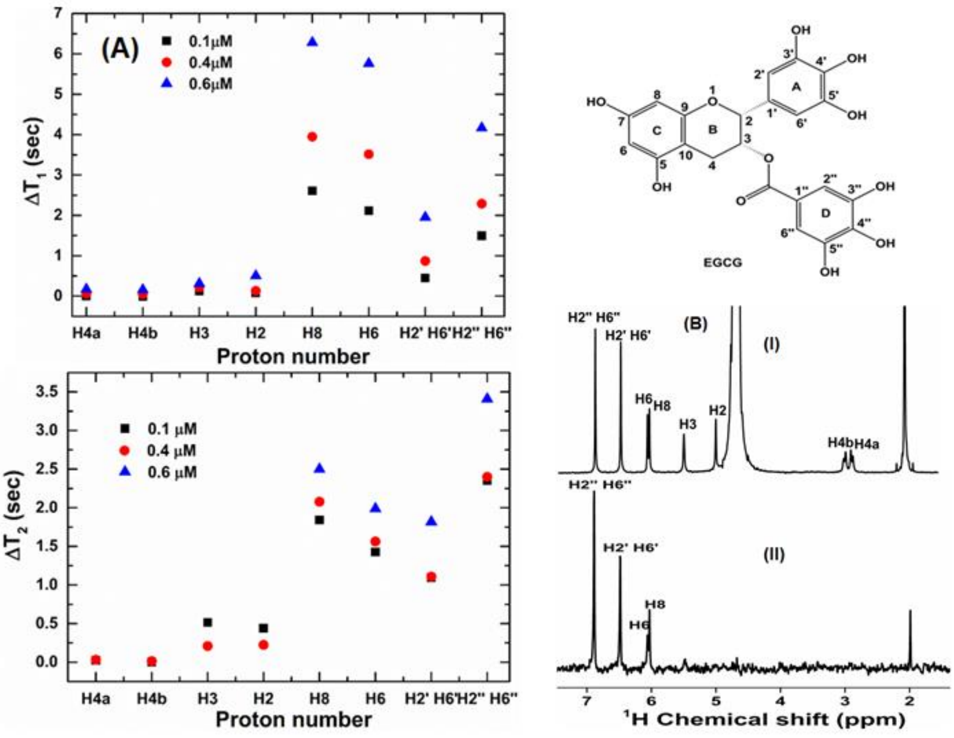


Figure 4 (A) ^{1}H T_1 and T_2 relaxation times of EGCG in the presence of different concentrations of collagen relative to EGCG (6 mM) alone. (B) 1D proton NMR of EGCG (6 mM) in the presence of collagen (0.6 μM) is shown in (I), while corresponding STD spectrum is displayed in (II).

To further probe the site-specific interaction of collagen with polyphenols, Model Collagen peptides (MCP) in its triple helical form has a molecular weight of 10 KD was used for studying its interaction with the polyphenols viz., GA, CA, EGCG, and TA. MCP chosen for the study mimics the structure and functionality of collagen. Earlier MCPs have been effectively used to understand the structure of collagen triple helix using biophysical techniques. The challenges in crystallizing and performing multidimensional NMR on collagen have been offset in part by the success of X-ray crystallography and NMR studies on peptides. Our NMR spectroscopic studies reveals that polyphenols interact with strongly with ionic amino acids flanked by proline or hydroxyproline amino acids. Further, we observe that polyphenols interact with the triple helical structure of MCP but not with its monomeric conformation. The detailed evidence on the site-specific interaction of polyphenol with triple helical structure will be made in the oral presentation.

ACKNOWLEDGMENTS

The use of the Bruker 400 MHz solution NMR spectrometer at CSIR-CLRI NMR facility is gratefully acknowledged. The authors also would like to acknowledge the financial support from the STRAIT under the XII five year plan project of CSIR-CLRI.

REFERENCES

1. Ramachandran G N, In: Treatise on Collagen, Academic Press, New York, 1967.
2. Nimni M E, Harkness R D, In: Collagen, Nimni, M. E, ed, CRC Press, Boca Raton, 1, 1988, 1- 4.
3. Ramachandran G N, Chandrasekaran R, Inter chain H-bonds in bound water molecules in the collagen triple helix. *Biopolymers*, 1968, **6**, 1649-1658.
4. Brodsky B. Hydrogen bonding in triple helix. *Proc. Indian. Acad. Sci*.1999, **111**, 13-18.
5. Brodsky B, Ramshaw J A M, The collagen triple- helix structure. *Matrix Biol*. 1997, **15**, 545-554.
6. Okuyama K, Miyama K, Mizuno K, Bächinger H P, Crystal structure of (Gly-Pro-Hyp)$_9$: Implications for the collagen molecular model. *Biopoly.* 2012, **97**, 607-616.
7. Gayatri R, Rajaram R, Ramasami T, Inhibition of collagenase by Cr(III): its relevance to stabilization of collagen. *Biophys. Biochim. Acta*. 2000, **1524**, 228-237.
8. Madhan B, Krishnamoorthy G, Rao J R, Nair B U, Role of green tea polyphenols in the inhibition of collagenolytic activity by collagenase. *Int. J. Biol. Macromolec.*2007, **41**,16-22.
9. Madhan B, Fathima N N, Rao J R, Subramanian V, Nair B U, Ramasami T, Hydration in matrix stabilization of collagen fibers: Relevance to mechanistic insight into tanning. *J. Ame. Leath. Chem. Assoc.*2003, **98**, 263-272.
10. Reddy R R, Phani Kumar B V N, Shanmugam G, Madhan B, Mandal A B, Molecular Level Insights on Collagen–Polyphenols Interaction Using Spin–Relaxation and Saturation Transfer Difference NMR. *J. Phys. Chem. B.* 2015, **119**, 14076-14085.
11. Mayer M, Meyer B, Group Epitope Mapping by Saturation Transfer Difference NMR To Identify Segments of a Ligand in Direct Contact with a Protein Receptor. *J. Am. Chem. Soc*. 2001, **123**, 6108–6117.

FLS O-02

MEASURING THE HERITABILITY OF LEATHER TRAITS IN SHEEP AND DEERSKIN

Geoffrey Holmes*, Sue Cooper, John McEwan, Kathryn M. McRae, Rayna Anderson, Jamie Ward

New Zealand Leather and Shoe Research Association (Inc.), PO Box 8094, Hokowhitu, Palmerston North, 4446, New Zealande-mail: info@lasra.co.nz

AgResearch Ltd, Invermay Agricultural Centre, Puddle Alley, Private Bag 50034, Mosgiel, 9053, New Zealand, e-mail: john.mcewan@agresearch.co.nz

This study explored the genetic variability in the New Zealand sheep and deer populations for a number of important skin traits.

Three hundred and five slaughtered progeny of Focus Genetics sheep-meat sires were evaluated for a number of pelt traits. DNA profiles were used to identify the skins collected post slaughter, the animals having previously been genotyped with Illumina 600K HD SNP chips as part of separate FarmIQ meat quality project. Considerable phenotypic variation for pelt traits was observed with around 30% of pelts identified as suitable for high value shoe leather production. Several key pelt traits associated with high value leather production were found to be moderately to highly heritable. This preliminary data will contribute to a larger study investigating if suitable lamb pelts can be bred or identified for use as high value shoe leather.

A more traditional approach was applied to deerskins. Slaughtered eleven-month-old progeny (n=310) from terminal (wapiti crossbred) and maternal (red) sire types were evaluated for 18 different quantitative and qualitative traits throughout processing to pearl-crust leather. For all traits except evenness grade of the pearl-crust leather, the relationship with pre-slaughter live weight covariate was significant ($p<0.05$) and positive. Sire had a significant effect ($p<0.01$) on eight traits including critical strength and finished-leather attributes ($p<0.01$) indicating genetic variability in these traits although larger numbers would be required for accurate heritability estimates.

This study provides a first insight into genetic variability in the properties of sheep and deerskins, and has wide-ranging benefits for other animal types; including cattle, where SNP chip technology is in an advanced stage of development.

Keywords: Heritability, leather, traits, phenotype

1. INTRODUCTION

The physical properties of lambskins have been measured in a number of studies (Milnes et al., 1977, Haines, 1981, Ward et al., 1965), as they are very important in determining the uses to which lambskin leather can be put. Traditionally, they have been used for clothing, a relatively low-value use, but if strength was improved they could be moved into the more lucrative and dependable footwear market. In previous studies of large flocks of sheep (unpublished work) LASRA has identified significant variations between milk lambs (less than 3 months old) and more mature lambs (6-9 months), and between black-face and white-face sheep of the same age. This suggests there may be both genetic and age-related factors at play.

Estimates of the genetic parameters for skin and leather traits in mammals are extremely rare in the literature. In sheep Scobie et al (2006) investigated the relationship between skin wrinkles and leather quality finding that selecting animals without wrinkles improved pelt quality. Icelandic lambs were found to be particularly suitability for use in reverse fur clothing due to their relatively light weight and lower frequency of environmental faults such as insect bites (Hjartarson, 2000). Woolskin traits in Icelandic sheep were reviewed by Adalsteinsson (1983), and wool quality scored in a similar way to Gotland sheep, with the curl, lustre and wool density found to have low to moderate heritability across three studies (Adalsteinsson, 1983). Eythorsdottir (1999) investigated a number of pelt traits in an Icelandic sheep breed, including thickness and double hiding in salted and tanned skins, with good correlation between traits measured on salted and tanned skins. Eythorsdottir estimated heritability scores for wool density (0.31) and lustre (0.28) on autumn lamb pelts. Age was found to have a negative impact on wool quality traits in all studies.

In subsequent work Nasholm and Eythorsdottir (2011) reviewed the characteristics and utilisation of special pelt products from Icelandic, Swedish (Gotland) and Karakul breeds of sheep, focusing on specific pelt traits associated with these breed, as well as Australian and New Zealand pelts, which are characterised by large quantities of Merino and Merino-derived breeds in Australia and a variety of different sheep breeds for woolskins and leather (Passman and Sumner (1987)) in New Zealand, and found that pelts with high loose wool bulk were best suited for double face production but not as well suited to leather tanning.

Similarly in cattle an autosomal recessive trait called vertical fibre hide defect (VFHD), which is a structural fault in collagen fibre orientation which leads to poor interweaving and weakness has been studied in Hereford cattle. VFHD phenotypes were diagnosed in pairs of offspring and dams by Cundiff et al (1987) and are broadly reflective of numerous analogous skin conditions in humans.

Perhaps the major difference in sheep is that hair sheep normally have better quality pelts than wool sheep (Oliveira et al., 2007, Cloete et al., 2000, Carneiro et al., 2010, Jacinto et al., 2004) although results can be variable. Jacinto et al., (2004), found significant improvements in the tensile strength and load of the skins of non-wool Morada Nova sheep compared with those from the Ideal wool-on breed, the differences being partially explained by the relatively thicker grain layer on the wool-on sheep and increased follicular and glandular density. In a study by Teklebrhan et al, (2012) physico-mechanical strength properties were measured on both indigenous Ethiopian and cross-bred sheep, which had their diet closely monitored. The cross-bred sheep were Ethiopian sheep, sired by Dorper sheep imported from South Africa. Dorper sheep skins are highly regarded for their properties for clothing and gloving production (Terblanche, 1979). In this case, the cross-bred skins were found to have similar chemical characteristics and be of similar strength to those of the indigenous sheep, although native breeds tended to produce slightly higher quality leather.

The purpose of the two studies reported here was to investigate whether different physical skin properties, identified in the part-processed and resultant leathers were related to the genetic make-up of sheep and deer, two economically important species for New Zealand. If genetic variability exists, this can be exploited to improve the quality of deer and lamb pelts; and thereby increase their value to farmers and skin processors.

2. MATERIAL AND METHODS

Collection and processing of deerskins

The first of the two trials was the more traditional evaluation of traits in red deer skins (Cervus elaphus spp.) as part of the Deer Progeny Test (DPT), relying on progeny DNA pedigree information extracted from the DEERSelect database for analysis (Ward et al., 2014). It was conducted across three commercial deer farms in New Zealand between 2011-2013 years with the primary aim of genetic improvement, while reducing variation in important traits related to meat and skin quality. The skin traits reported here were measured on the 2011 birth cohort on hinds (N = 285) of the red deer subspecies from two different age classes; rising-three-year-old (R3) and mixed age (MA) (rising-four-year-old and above) on Invermay farm (Otago) and Whiterock Station (Canterbury) (Ward et al., 2015).

All progeny from each farm were transported and slaughtered on a single occasion during October 2012, Animals were kept in lairage overnight with access to water and separated by mob/sex, then slaughtered the following day (Ward et al., 2015). Following removal of the skin post-slaughter at Alliance Group Makarewa, they were screen-washed with cold water to cool for two minutes. They were drained, salted using a standard commercial recipe, stacked on wooden pallets and stored covered with plastic for approximately 12 months. Subsequently, the salted skins were wet back and processed through the commercial processing plant at New Zealand Light Leathers Ltd. (Washdyke, New Zealand), following a conventional deer process, used for bulk production, with the only major difference being that the skins were undyed and left unshaved in the crust state prior to dry drumming.

Collection and processing of lambskins

The second trial was conducted on sheep progeny born in 2014 as part of the FarmIQ Awapai Progeny Test from terminal sire composites (Primera), mated to a variety of maternal breeds but predominantly Highlander ewes (Brito et al., 2015). The ewes were mob mated in large groups, with sires assigned to progeny through DNA pedigree. There were 75 sires represented in the data, with an average of 5 progeny per sire. All progeny were genotyped using the Ovine Infinium® HD SNP BeadChip (Anderson et al., 2014). Both male and female progeny were slaughtered in February 2015. Following removal of the skin post-slaughter, lamb skins were collected, and sent to Tomoana Pelt Processors (TPP), Whakatu, for processing. At TPP the green skins were fleshed, individually labelled, and a tissue sample collected for DNA identity matching. The skins were processed through to the pickle stage at the fellmongery using a standard commercial process and set aside at pickle grading for return to LASRA where they were converted to crust leather using a standard process known to provide good strength properties.

Grain strain was measured on the depickled pelts after treating with Sortassist®, Stahl Holdings BV, a pH-dependent blue pigment that highlights grain defects. They were then photographed and scored for the extent and severity of grain strain on the flanks on a scale of 0 (none) to 4 (the most severe/extensive seen). The two flanks of each pelt were assessed separately and the scores added to give a minimum pelt score of 0 and a maximum pelt score of 8. Further testing was conducted on the crusted skins after they were staked and toggled. Samples for physical testing were cut out using press knives on a hydraulic press and conditioned at 20°C and 65% relative humidity (RH) for at least 24 hours before testing. Thickness of leather was measured in the neck, backline, midside area and belly. Leather thickness was measured using a Specht leather thickness gauge. Tensile strength and percentage extension of the leather was measured according to International Standard ISO 3376:2002 using an Instron® Model 4467 Universal Testing System. Testing was performed in parallel and perpendicular in relation to the backline in quadruplicate on each skin, the results being averaged. Tear strength of the leather was measured according to International Standard ISO 3377-2:2002. Tests were performed in parallel and perpendicular in relation to the backline in quadruplicate for each skin using the same Instron tensile testing machine as above. The results were expressed both as the absolute force required to tear the leather (N) and as the force per unit thickness of the sample (N/mm), and the values for each skin averaged to give a skin value. Grain strength and extensibility was measured in triplicate for each skin using the ball burst test, International Standard ISO 3379:1976. The results for each skin were averaged to give a skin value. Results were expressed as Newtons (N) of force and mm of extension. Finally, evaluation of flatness was carried out by an experienced assessor, on a scale of 0 (completely flat) to 4 (extreme bumpiness of the surface) on the crusted material. Because values vary widely over the skin, with the neck region usually being significantly less flat than the rest of the skin, the neck area, the butt and the rest of the skin were assessed separately. The three figures were then added to give a whole skin grading between 0 and 12.

To match the skin number to individual animal ID, DNA was extracted from the tissue samples obtained from the lambskins. A Sequenom parentage panel was run on each sample (Clarke et al. 2014), and these results were used to match to animal ID using stored HD genotypes from the same animals.

3. RESULTS AND DISCUSSION

Deerskin data

Data were analysed using least squares means (LSM) analysis to test significance of the skin traits and responses of the various factors (i.e., farm, year, mob, sex and sire type) and predict overall responses of these factors including sire. Pre-slaughter live weight was independently fitted as a covariate. Sire had a significant effect ($p<0.01$) on eight traits; all six crust-leather-tearing traits, pearl-crust leather evenness grade and wet-blue thickness, measured mid-back. Range summaries of these traits with significant sire-effects are presented in Table 1. Farm had a significant effect ($p<0.01$) on eight traits ranging from wet-blue size and thickness, to crust leather strength. Wet-blue area, width behind fore legs, thickness mid-neck and mid-side were all significantly positive ($p<0.01$) for the Invermay Farm. Crust leather strength; parallel, perpendicular and mean were all highly significantly ($p<0.001$) positive for the Whiterock Station progeny. Crust leather tear strength perpendicular to the spine and wet-blue thickness mid-side were the only traits on which mob had a significant effect ($p<0.05$). The responses for these two traits were negative for progeny of R3 hinds. There was no significant effect of sex ($p<0.05$) on any of the traits measured. The discrete trait data (i.e. rank and grade) presented quite skewed distributions in some cases. Wet-blue quality was the most skewed with 204 skins in the top grade, 73 in the middle and only eight in the bottom grade.

Table 1 Deer-skin traits of the 2011 deer progeny test birth cohort predicted by least squares means analysis where sire (n=14) was a significant effect in the model.

Trait name	**N progeny**	**Mean progeny response**	**Sire mean response**	**Sire maximum response**	**Sire minimum response**	**Sire response std**	**Sire response coefficient of variance %**	**Range of sire responses**	**SireID and Random (p score)**	**Covariate Weight Pre-slaughter (p score)**	**Covariate response**	**Covariate response % mean**
Wet-blue skin thickness at middle of back (mm)	270	1.95	1.95	2.07	1.84	0.07	3.6	0.23	<0.01	<0.0001	0.01	0.5
Crust-leather tear-force parallel to spine (N)	282	213	215	235	197	11	5.1	37.8	<0.0001	<0.0001	1.84	0.9
Crust-leather tear force perpendicular to spine (N)	282	160	161	178	146	8.9	5.5	32.5	<0.0001	<0.0001	1.4	0.9
Crust-leather mean tear force of both axis (N)	282	186.1	188.3	206.5	171	9.96	5.3	35.5	<0.0001	<0.0001	1.62	0.9
Crust-leather tear strength parallel to spine (N/mm)	282	108.4	110	113.7	104	2.6	2.4	9.6	<0.01	<0.0001	0.26	0.2
Crust-leather tear strength perpendicular to spine (N/mm)	282	87.2	88.2	93.9	81	3.37	3.8	12.77	<0.0001	<0.01	0.18	0.2
Crust-leather mean tear force of both axis (N/mm)	282	97.8	98.86	104	92.3	3.03	3.1	11.7	<0.0001	<0.0001	0.22	0.2
Pearl crust evenness grade (Rank 1-3)	282	1.76	1.78	2.14	1.47	0.2	11.2	0.67	<0.01	<0.05	0.01	0.5

Lamb pelt data

Data cleaning consisted of removal of records with duplicate animal IDs. For traits where multiple values were recorded, trait average was used. Considerable phenotypic variation for pelt traits was observed with around 30% suitable for high value shoe leather production.

Parsimonious models for fixed effects and covariates were identified for each trait separately via backwards elimination using the GLM procedure (SAS Inst. Inc., Cary, NC). Fixed effects tested were sex, weaning mob (WWTm), pre-slaughter weight (PRESLTWT), carcass weight (CWT), and depth of tissue 110 mm off the mid line in the region of the 12th rib (CGRM). Sex and carcass weight were significant fixed effects for multiple traits (Table 2). The final dataset used in the analysis contained records for 287 (138 male and 149 female) lambs (Table 2). Variance components were then estimated using restricted maximum likelihood (REML) procedures fitting an animal model in ASReml (Gilmour et al., 2015), for fixed effect models previously defined along with the genomic relationship matrix (GRM) estimated in GenABEL (Aulchenko et al., 2007) using HD genotypes. Heritabilities were estimated via univariate analyses on the respective traits.

Table 2 Descriptive statistics, repeatability and heritability for individual trait analyses in sheep. Significant values are shown in bold. All mixed models included animal as a random effect.

Trait	**N**	**Mean ± SD**	**Range**	**Heritability**	**Fixed effects**
Neck	287	2.8 ± 0.8	0.5 - 4	0.13 ± 0.16	sex
Butt	287	2.2 ± 1	0 - 4	0.21 ± 0.17	sex
Belly	287	1.8 ± 0.9	0 - 4	0.23 ± 0.18	-
Overall	287	6.8 ± 2.4	1 - 12	0.15 ± 0.17	sex CGRM
Tear parallel (N/mm)	283	47.7 ± 6.6	33.8 - 78.3	0.26 ± 0.18	sex CWT
Tear perpendicular (N/mm^2)	283	47.3 ± 58.7	28.1 - 1026.5	0.02 ± 0.12	-
Tensile parallel ext (mm)	286	35.6 ± 6.1	23.4 - 92.3	NE	-
Tensile parallel (N/mm^2)	286	**161.4 ± 24.2**	**105 - 245.7**	**0.85 ± 0.20**	**sex**
Tensile perpendicular ext (mm)	286	57.6 ± 11	32.4 - 90.4	NE	PRESLTWT
Tensile perpendicular (N/mm^2)	286	110.4 ± 17.4	62.3 - 196.4	0.35 ± 0.20	sex
Lastometer load (N)	285	**26.5 ± 6**	**12 - 44**	**0.54 ± 0.20**	**CWT**
Lastometer ext (mm)	285	8.9 ± 0.6	6.2 - 10.8	0.12 ± 0.15	CWT
Strain	287	**3.4 ± 1.8**	**0 - 8**	**0.86 ± 0.21**	**PRESLTWT CWT**

Note: NE = Not estimable

In general females and lighter lambs had pelts with lower strength characteristics. Several key pelt traits associated with high value leather production were moderately to highly heritable; three of the traits examined, tensile parallel, lastometer load, and strain, appear to have a significant genetic component. It must be noted that the lambskin results use only 287 animals (whose skins could be uniquely attributed to the individual), and therefore must be interpreted with caution. Further work is justified to more precisely estimate the genetic parameters, investigate year to year variability, examine a wider range of sire breed and define the genetic relationships between pelt traits and production traits in sheep with greater precision. This will allow a formal evaluation of the potential for in-plant and genetic selection to produce lines of pelts suitable for shoe leather production.

4. CONCLUSION

The results from both of these studies indicate that there is genetic variability in the New Zealand sheep and deer populations for a number of important skin traits, which provides useful knowledge for predicting the properties of skins from animals of known genetic profile.

It is highly unlikely that farmers will breed either sheep or deer for their skin properties. Dual-purpose sheep breeds in New Zealand derive most of their value from the wool and meat they produce, with the skin being a by-product. Future work to identify traits of benefit to the farmer (such as weaning or carcass weight) that have a positive correlation with traits of strength in the animal's skin, would mean that there was an additional purpose and reason to actively improve these properties in the animal's genetic profile.

In lamb skins, several key pelt traits associated with high value leather production were found to be moderately to highly heritable, including grain and tensile strength. This preliminary data will contribute to a larger study investigating if suitable lamb pelts can be bred or identified for use as high value shoe leather. This study is an important milestone, as to our knowledge it is the first in which SNP-chip technology has been used to investigate skin and leather traits

Much the same principles apply to deerskins. While the hair of deer has no value, they are purposely bred for meat with by-products such as the pelt providing additional value. There was a significant sire effect, indicating a genetic component, for a number of important deerskin quality traits including tear strength, pearl-crust-evenness grade and mid-back thickness. These traits could be genetically selected for if a suitable cost-effective way of tracing finished skins to individual animals could be established. Environmental factors of farm and mob (effectively age-of dam) are also important factors in the quality of deerskins. These factors could offer the opportunity to select higher quality batches of skins based on farm information rather than fully tracing skins through the slaughter and tanning process.

5. ACKNOWLEDGEMENTS

The sheep flock involved in this study was from a FarmIQ funded progeny test program. We also acknowledge New Zealand Light Leathers Ltd, Silver Fern Farms Ltd and Tomoana Pelt Processors Ltd for their assistance in collecting, sorting and processing the skins in these two trials.

6. REFERENCES

1. Milnes RH, Peters GP, The quality of some New Zealan deerskins. New Zeal J Agr Res. 1977, 199-201.
2. Haines BM, Breed differences in cattle hides. JLSTC. 1981, 65, 70-78.
3. Ward AG, Brooks FW, Relationship of mechanical properties to structural variation through the thickness of skin and leather (part I), JSLTC. 1965, 49, 312-323.
4. Unpublished LASRA Milestone Report 07MR/LA05, Meat & Wool New Zealand. 2008
5. Anderson R, McEwan J, Brauning R, Kijas J, Dalrymple B, Worley K, Daetwyler H, Heaton M, Van Stijn T, Clarke S, Baird H, Khan A. 2014 Development of a high density (600K) Illumina ovine SNP chip and its use to fine map the yellow fat locus (https://pag.confex.com/pag/xxii/webprogram/Paper10725.html)
6. Aulchenko YS, Ripke S, Isaacs A, van Duijn CM: GenABEL: an R library for genome-wide association analysis. Bioinformatics 2007, 23(10):1294-1296.

7. Brito LF, Miller SP, Clarke SM, Dodds KG, Bain WE, Lee MA, Pickering NK, McEwan JC. Genetic parameters for growth carcass and meat quality traits in New Zealand sheep. Proceedings of the New Zealand Society of Animal Production 75: 94-96
8. Clarke SM, Henry HM, Dodds KG, Jowett TWD, Manley TR, Anderson RM, McEwan JC. A high throughput single nucleotide polymorphism multiplex assay for parentage assignment in New Zealand sheep. PLoS ONE 9(4): e93392. doi:10.1371/journal.pone.0093392
9. Gilmour AR, Gogel BJ, Cullis BR, Welham SJ, Thompson R: ASReml User Guide Release 4.1 Structural Specification. In. Hemel Hempstead, HP1 1ES, UK: VSN International; 2015: 1-375.
10. Ward JF, Archer JA, Asher GW, Everett-Hincks JM, Mathias-Davis HM, Design and implementation of the Deer Progeny Test (DPT). Proceedings of the New Zealand Society of Animal Production. 2014. 74: 220-225
11. Ward JF, Archer JA, Mathias-Davis HM, Cooper SM, Crawford EM, Wheeler M, 2015. Evaluation of production traits of red deer skins in the Deer Progeny Test. Proceedings of the New Zealand Society of Animal Production 75: 114-118
12. Scobie DR, Young SR, O’Connell D, Eythorsdottir E, Skin wrinkles of the sire adversely affect Merino and Halfbred pelt characteristics and other production traits Aust. J. Exp. Agric. 2005, 45, 1551-1557.
13. Hjartarson Þ. Skinna. Skinna : saga sútunar á Íslandi. Safn til iðnsögu Íslendinga / ritstjóri Jón Böðvarsson, 2000, Reykjavík : Hið Íslenzka Bókmenntafélag,
14. Adalsteinsson S, Inheritance of colours, pelt characteristics and skin quality traits in North European sheep breeds: a review. Livest. Prod. Sci. 1983,10, 555-567.
15. Eythorsdottir E, Genetic variation in woolskins quality of Icelandic lambs. Livest. Prod. Sci 1999,57, 113-126.
16. Nasholm A, Eythorsdottir E, Characteristics and utilization of sheep pelts. Small Ruminant Res. 2011, 182-187.
17. Passman A, Sumner RMW, Effects of breed and age at slaughter on leather produced from export lambs reared in hill country. N.Z. J. Exp. Agric. 1987, 15, 309-316.
18. Cundiff LV, Inheritance of vertical fiber hide defect in cattle. J. Hered. 1987, 78 (1), 24-28.
19. Oliveira RJF, Costa RG, Sousa WH, Medeiros AN, Dal Monte MAB, Aquino D, Oliveira CJB, Influence of genotype on physico-mechanical characteristics of goat and sheep leather. Small Ruminant Res. 2007, 73, 181-185.
20. Cloete SWP, Snyman MA, Herselman MJ, Productive performance of Dorper sheep. Small Ruminant Res. 2000, 119-135.
21. Carneiro H, Louvandini H, Paiva, Macedo F, Mernies B, McManus C, Morphological characterization of sheep breeds in Brazil, Uruguay and Colombia. Small Ruminant Res.2010, 58-65.
22. Jacinto MAC, da Silva Sobrinho AG, Costa RG, Anatomical-structural characteristics of wool-on and non-wool sheep skins related to the physical mechanical leather aspects. R. Bras. Zootec. 2004, 33, no.4.
23. Teklebrhan T, Urge M, Mekasha Y, Skin/ leather quality of indigenous and crossbred (Dorper x Indigenous) F1 sheep, Livestock Res Rural Dev, 2012, 24 (4).

FLS O-03

CHROME-TANNED LEATHER SHRINKAGE PROBED WITH MODULATED TEMPERATURE DIFFERENTIAL SCANNING CALORIMETRY

Richard L. Edmonds

Leather and Shoe Research Association, Palmerston North, 4412, New Zealand
Email:richard.edmonds@lasra.co.nz

In this work, the relatively new technique of modulated temperature differential scanning calorimetry (MTDSC) was used to investigate the shrinkage reaction of chrome-tanned leather. Differential scanning calorimetry (DSC) is in common use for the investigation of the leather shrinkage reaction. However, by modulating the temperature treatment of the sample rather than treating it to the flat temperature ramp normally applied in DSC, the transitions that occur can be separated into reversing and non-reversing transitions. In this work, the chrome shrinkage reaction is probed using MTDSC and the shrinkage reaction characterised as wholly non-reversing. This contrasts with glass transitions and melting transitions, which are characterised as reversing.
Keywords: DSC, MDSC, shrinkage, collagen denaturation reaction

INTRODUCTION

For a long time differential scanning calorimetry (DSC) has been an important tool for measuring the shrinkage reaction of skin and leather (Bao et al. 2007; Chen and Shan 2008; Chen and Shan 2009; Ding et al. 2008; Heath et al. 2005; Kronick and Buechler 1986; Luo et al. 2011; Madhan et al. 2003; Tang et al. 2003).

DSC measures the difference in energy input between the sample and a blank reference as the sample reference pair are treated to a temperature profile (typically a simple ramp). The energy of transitions are measured and can be illustrated as a thermogram.

By adding a modulated temperature profile to the ramp additional information can be gained from the resulting experiments (Reading and Hourston 2006). The addition of a changing rate of temperature allows for separation of thermal transitions which depend of absolute temperature (kinetic transitions, such as irreversible chemical reactions) from those which also depend on the rate of temperature change (dynamic transitions, such as reversible melting).

Earlier work of leather has indicated that at low scan rates of 0.5°C/min the reaction has a reasonable fit to first order decay(Liu and Li 2010; Liu and Li 2015). This would imply that for these low scan rate experiments no reversing signal would be expected. Recent application of MDSC to a selection of tanned and untanned skin samples found that this was the case (Edmonds 2016).

In this work the methodology for application of MDSC to leather samples is briefly discussed and then applied at a selection of scan rates in order to directly measure the reversing/non-reversing nature of the chrome tanned collagen shrinkage reaction.

MATERIAL AND METHODS

The methodology of the application of MDSC to leather samples has been recently described. (Edmonds 2016). The method is briefly described here;

Samples of wet blue hide obtained from a cooperating hide tannery were initially prepared as per conventional DSC with thin (50µm) sections of hydrated wet blue cut from a block and loaded into an aluminium DSC pan to produce a sample weight of approximately 10mg. Samples were then hermetically sealed to await testing in the MDSC. Whereas DSC has one parameter of operation (the scan rate), MDSC has three parameters of operation: The overall scan rate, the modulation amplitude, and the modulation period. The process for determining those parameters has been previously described for the purpose of the application of this technique to leather samples in (Edmonds 2016). It was suggested that a scan rate of 0.5°C/min, and amplitude of 0.12°C and a period of 2 minutes be applied. In this work, the amplitude and period are kept constant and the overall scan rate adjusted in order to attempt to detect any potential reversing transition that might be expected at higher scan rates.

Results and discussion

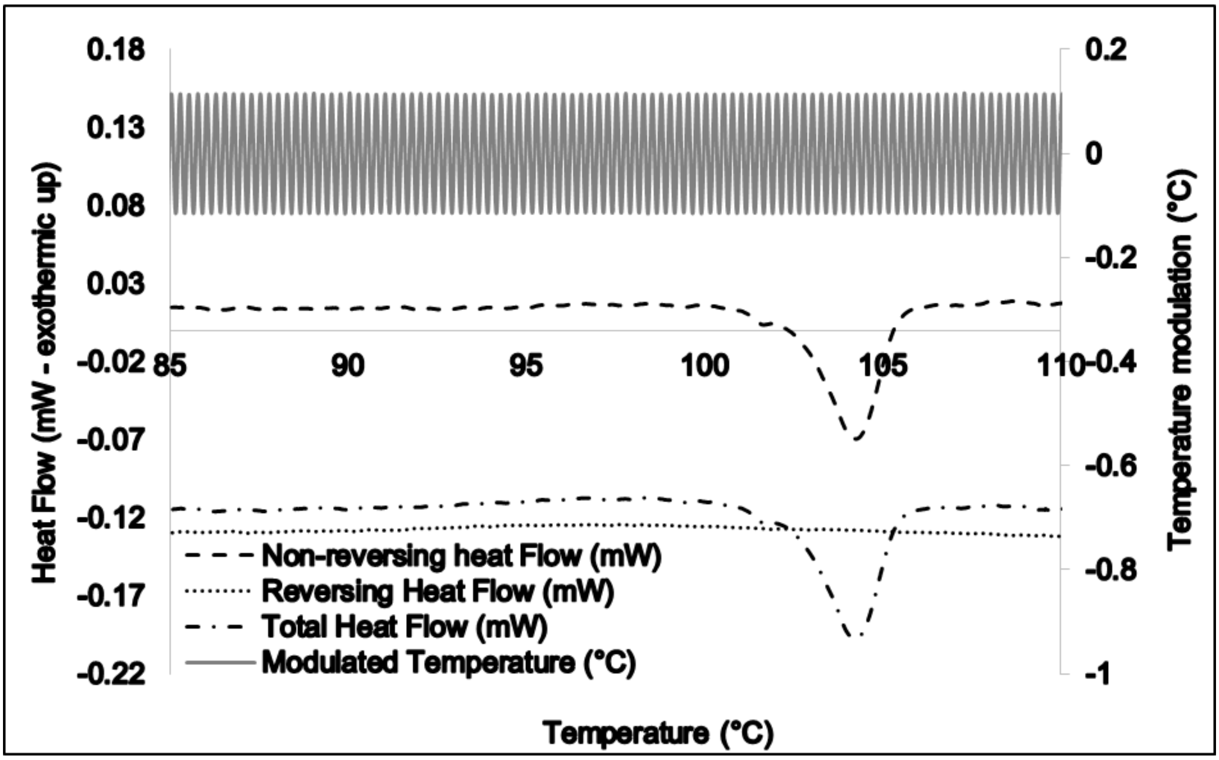


Figure 1: MDSC thermogram of chrome tanned wetblue scanned at 0.25°C/min. Note no peak in the reversing signal at this scan rate.

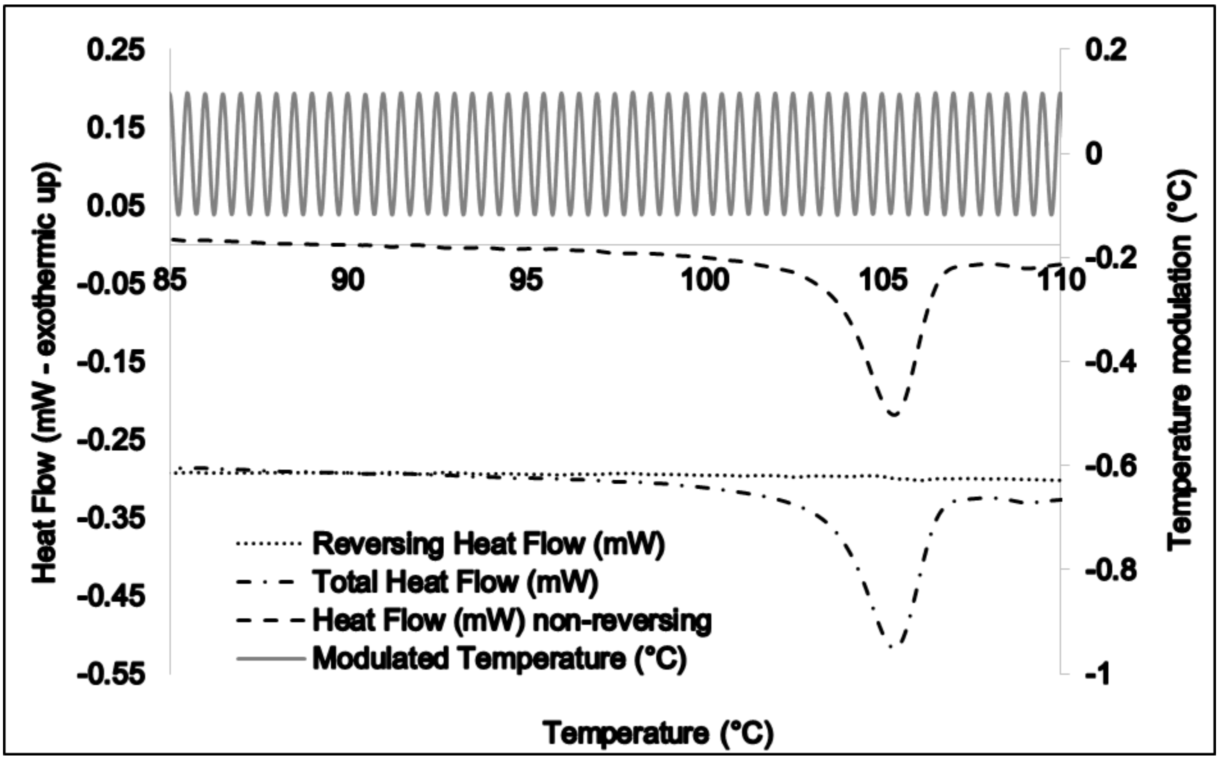


Figure 2: MDSC thermogram of chrome tanned wetblue scanned at 0.50°C/min. Note no peak in the reversing signal at this scan rate.

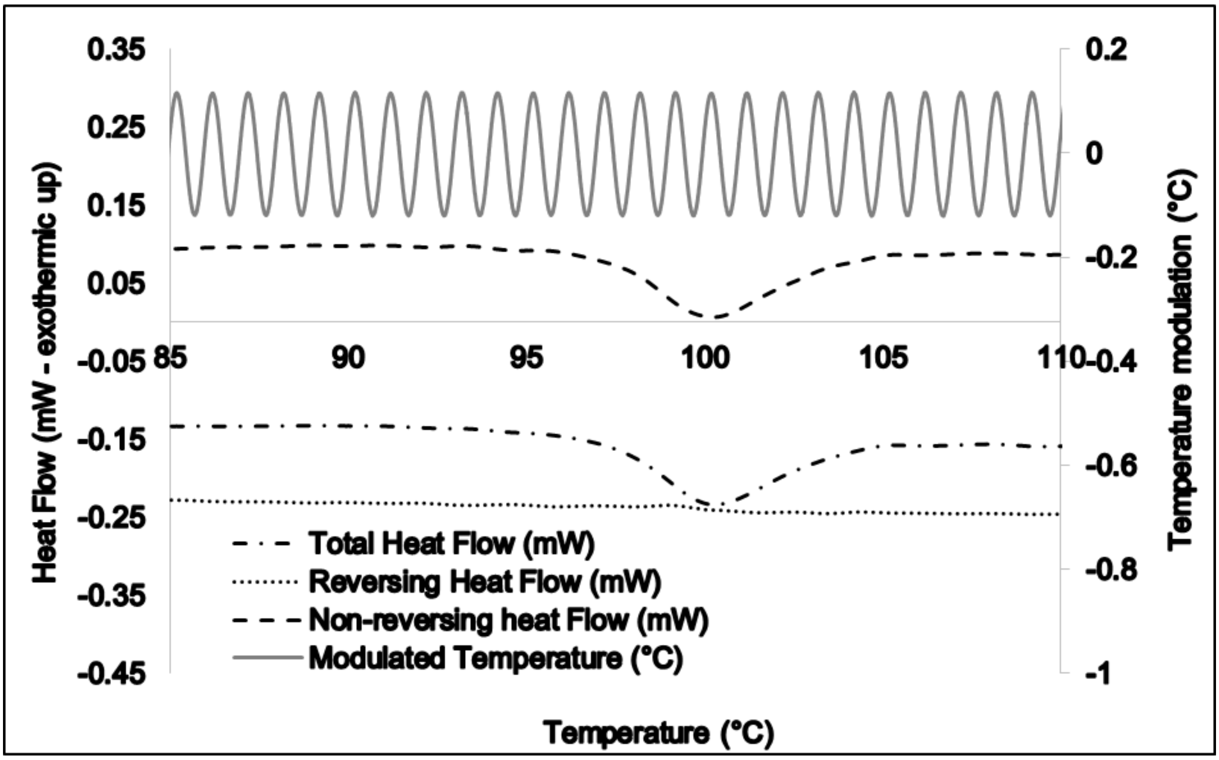


Figure 3: MDSC thermogram of chrome tanned wetblue scanned at 1.00°C/min. Note no peak in the reversing signal at this scan rate.

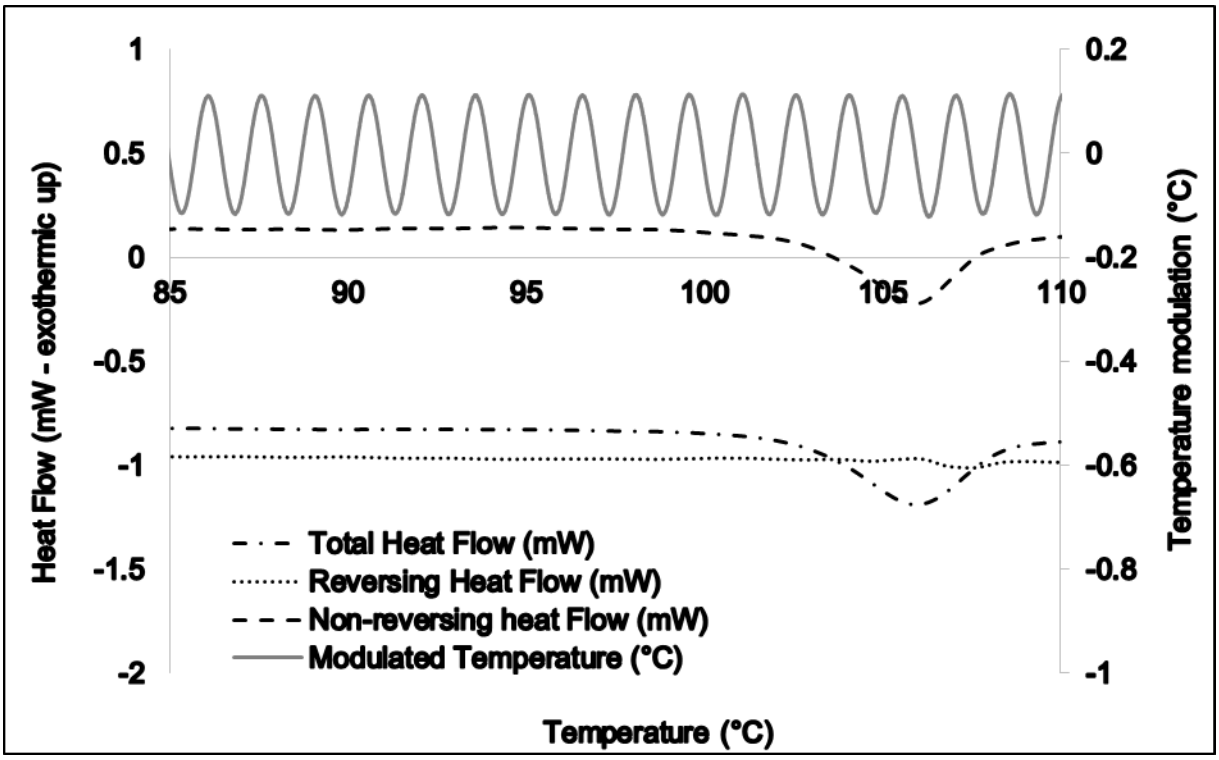


Figure 4: MDSC thermogram of chrome tanned wetblue scanned at 1.50°C/min. Note the small peak in the reversing signal at this scan rate.

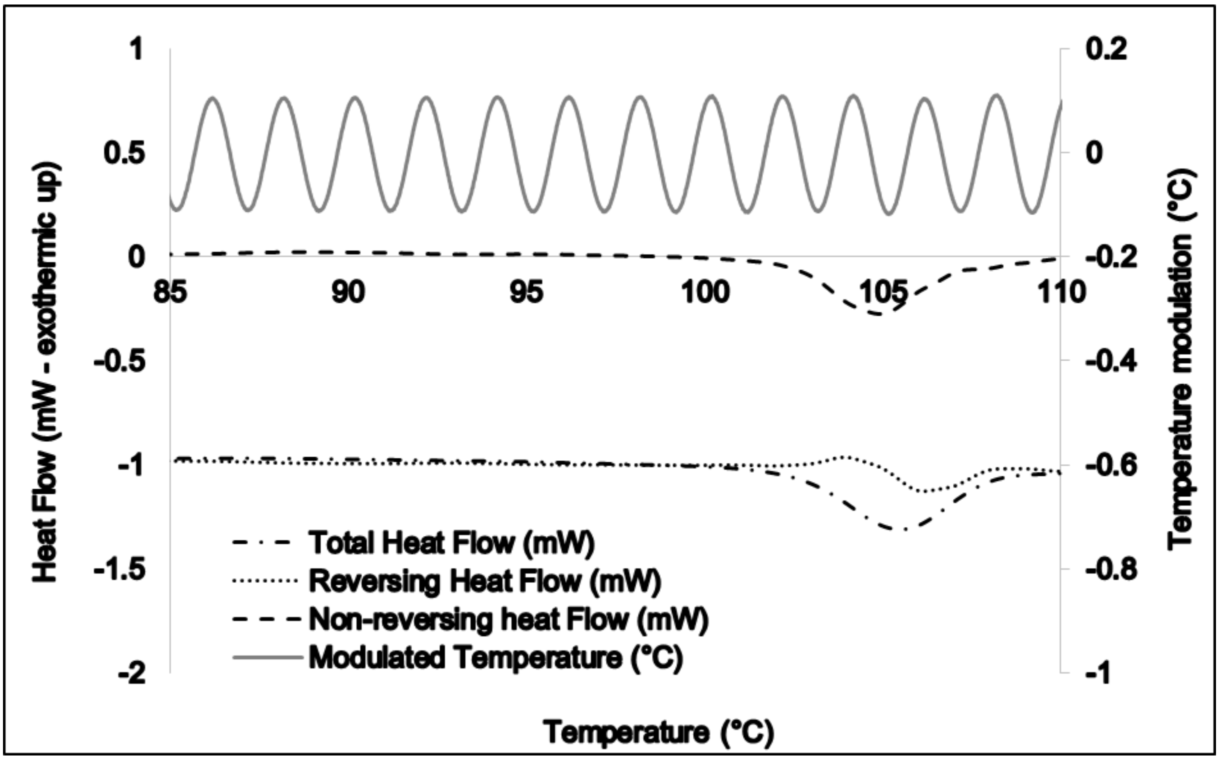


Figure 5: MDSC thermogram of chrome tanned wetblue scanned at 2.00°C/min. Note the peak in the reversing signal at this scan rate.

As found previously, the reversing peak for the sample scanned at lower scanning rates (<=0°C/min) is negligible, whereas a significant reversing peak was observed at higher scan rates (>1°C/min).

However, the maximum scan rate is limited by the ability of the analysis system to resolve the reversing and non-reversing signals from the modulated result data. In order to resolve the transition there needs to be at least 4 periods of modulation within the transition of interest. In the case of the higher scan rates investigated here there are only barely enough modulations within the transition and it may be possible that the peaks observed here in the reversing signal are an artefact of the analysis technique. Further work will need to be carried out to confirm the nature of the reversing peak at higher scan rates.

It should also be noted that a possible reversing transition does not necessarily directly link to a reversible reaction step. The influence of reaction mechanism steps on the reversing signal is complex. The relationship between reversible reaction steps and the reversing signal will therefore require more analysis in order to reconcile the observed results.

CONCLUSION

In this work, the influence of scan rate on the reversing component of leather shrinkage has been investigated. At a scan rate of 1°C/min and below leather shrinkage has a negligible reversing component, whereas at higher scan rates a significant reversing component was observed. Further analysis will be required to link the mechanism of leather shrinkage to the results observed in this work.

ACKNOWLEDGEMENTS

The author would like to acknowledge the New Zealand Ministry of Business Innovation and Employment for funding this work within project LSRX0801, and the assistance of Fraser Stevens in operation of the MDSC.

REFERENCES

1. Bao, Y., Yang, Z. & Ma, J., Tanning mechanism of vinyl polymer/montmorillonite nanocomposite tannage, *J. Soc. Leather Technol. Chem.*, 2007, **91**(4) 162-167.
2. Chen, H. & Shan, Z.-H., Changes in hydrothermal stability of collagen with several catechin-metal compounds: A DSC study, *J. Soc. Leather Technol. Chem.*, 2008, **92**(3) 93-95.
3. Chen, H. & Shan, Z.-H., The reaction mechanism between collagen and phenol / oxazolidine E tanning matrices, *J. Soc. Leather Technol. Chem.*, 2009, **93**(1) 121-125.
4. Ding, K., Taylor, M.M. & Brown, E.M., Tanning effects of aluminum - genipin or vegetable tannin combinations, *J. Amer. Leather Chem. Assoc.*, 2008, **103**(11) 377-382.
5. Edmonds, R.L., Application of modulated temperature differential scanning calorimetry (MTDSC) on leather, *J. Soc. Leather Technol. Chem.*, 2016, **100**(6) 283-288.
6. Heath, R.J., Di, Y., Clara, S., Hudson, A. & Manock, H., The optimization of epoxide-based tannage systems - an initial study, *J. Soc. Leather Technol. Chem.*, 2005, **89** (3) 93-102.
7. Kronick, P.L. & Buechler, P.R., Effects of beaming and tanning on collagen stability, studied by differential scanning calorimetry, *J. Amer. Leather Chem. Assoc.*, 1986, **81**(7) 213-220.

8. Liu, W. & Li, G., Non-isothermal kinetic analysis of the thermal denaturation of type I collagen in solution using isoconversional and multivariate non-linear regression methods, *Polym. Degrad. Stab.*, 2010, **95**(12) 2233-2240.
9. Liu, W. & Li, G., Effect of chrome tanning on the thermal behavior of collagen fibers: A calorimetric and kinetic analysis, *XXXIII IULTCS Congress,* Novo Hamburgo, Brazil, Associação Brasileira dos Químicos e Técnicos da Indústria do Couro, 2015, #4
10. Luo, J., Feng, Y. & Shan, Z., Complex combination tannage with phosphonium compounds, vegetable tannins and aluminium tanning agent, *J. Soc. Leather Technol. Chem.*, 2011, **95**(5) 215-220.
11. Madhan, B., Nishad Fatima, N., Rao, J.R. & Nair, B.U., Molecular level understanding of tanning using an organo-zirconium complex, *J. Amer. Leather Chem. Assoc.*, 2003, **98**(11) 445-450.
12. Reading, M. & Hourston, D.J. *Modulated Temperature Differential Scanning Calorimetry;* Springer. Dordrecht, The Netherlands, 2006
13. Tang, H.R., Covington, A.D. & Hancock, R.A., Use of DSC to detect the heterogeneity of hydrothermal stability in the polyphenol-treated collagen matrix, *J. Agric. Food. Chem.*, 2003, **51**(23) 6652-6656.

INFLUENCE OF NAPHTHALENESULFONIC ACID DERIVATIVES ON THE DYEING PROPERTIES OF THE LEATHER. PART II

Olga Ballús*, Toñy Catalan, Ramón Palop, Ricardo Micó

Laboratorio de Curtidos. Cromogenia Units S.A, Email: oballus@cromogenia.com
Laboratorio de Curtidos. Quimipiel S.L, Email: tcatalan@quimipiel.com

The first part of this paper studied the influence of the composition of different types of naphthalenesulfonic acid derivatives, used in the neutralization phase, on certain characteristics of the leather when two dyes (Acid Black 210 and Acid Brown 83) were used separately.

This second part assessed the influence of these products on the same leather characteristics when equal parts of the same dyes were used together and an amphoteric dyeing auxiliary was added.

The results confirm that the greater the molecular weight of the naphthalenesulfonic derivative, the better the penetration of the dye mixture, and that this mixture behaves uniformly in terms of penetration and levelness. The addition of an amphoteric dyeing auxiliary led to outcome maximization.

Key words: auxiliary, amphoteric, naphthalenesulfonic, neutralization, dyeing

1. INTRODUCTION

After tanning the hide has an (approximately 4) acid pH and also a strong positive charge on account of chromium complex cationicity (Morera 2003; Soler 2000). During the neutralization process and by means of alkaline neutralizing agents, hide pH is increased to values close to 5-5.5. This operation, however, is insufficient by itself to facilitate the penetration and distribution of retanning agents, fatliquoring agents, and dyes (Heidemann 1993; Portabella 1962).

A change of charge in the hide, both on the surface and inside, is thus required through the addition of anionic auxiliary products, such as naphthalenesulfonic acid salts, to allow good penetration and distribution of further added products and consequently good physical and organoleptic properties (Palop et al. 2008; Ballús et al. 2014).

Anionic auxiliaries are naphthalenesulfonic acid derivatives with a relatively small molecular weight. On the one hand, they decrease the isoelectric point and thus facilitate the penetration of further added products; on the other hand, they may act as dyeing auxiliaries. When applied as dyeing auxiliaries they compete with the dye for fixation to the chrome tanned leather by decreasing substrate-dye interaction, and provide better levelness and usually decreased dyeing intensity (Covington 2009).

Non-ionic auxiliaries are also used to achieve good dyeing penetration. Because acid dyes are highly reactive in chrome tanned leathers, their penetration and levelness can be improved by adding this type of auxiliaries. Non-ionic auxiliaries form complexes with the dye, block its reactive points and decrease its reactivity. These compounds contain high quantities of oxygen atoms as well as a nitrogen group that provides them with weak cationicity. Occasionally, they may also increase dyeing intensity (Portabella 1962; Covington 2009).

The penetrating power of a dye depends on molecular weight, particle size, sulfonation, and solubility. Given the wide range of currently available dyes, its choice in this study was mainly based on its molecular weight. Two acid dyes with different molecular weights were selected. The dye with a higher molecular weight is expected to penetrate less than the dye with a lower molecular weight. This will allow assessing the influence provided by each auxiliary used.

In this study, the physical and chemical properties (molecular weight, number of sulfonic groups, and chain length) of several naphthalenesulfonic acid salts were related to the properties they provide to the leather, measured by anionicity penetration and dyeing properties (penetration, levelness and intensity) when a mixture of two acid dyes was added. The influence of an amphoteric auxiliary on dyeing properties was also assessed by measuring the above described parameters using a non-ionic amine.

Therefore, characterizing naphthalenesulfonic acids is essential. Reversed-phase high-performance liquid chromatography (RP-HPLC) allows to qualitatively determine the degree of condensation of each product, and gel permeation chromatography (GPC) allows determining the relative molecular weights of each product.

2. MATERIAL AND METHODS

Naphthalenesulfonics characterization

Six different products derived from naphthalenesulfonic acid were selected. RP-HPLC was first used for qualitative determination. Jasco HPLC model PU-2089J equipment was used, with a 5µm 25x0.46 Tracer Extrasil ODS2 column. A Jasco UV-2075 plus detector at a wavelength of 285nm was used. Pressure and mobile phase flow were set at 110-130Mpa and 1ml/min, respectively. A mixture of two solvents was used as the eluent solution: 0.01M of 99% TBAB in water and 1% in glacial acetic acid as solvent A; and 0.01M TBAB in 99% acetonitrile as solvent B. These solvents were used in different percentages in an elution program. At first 120 minutes a mixture of 80% of solvent A and 20% of solvent B were used, followed by 100% of solvent B during 40 minutes. Finally applied a mixture of 80% of solvent A and 20% of solvent B for 10 minutes.

Quantitative determination was performed by GPC with the same equipment, with a Shodex KS 803 column and a Jasco UV-2075 plus detector at a wavelength of 227nm, flow rate 0.8 ml/min, temperature 30ºC, using a Jasco CO-2065 plus oven. The eluent solution was prepared with acetonitrile and a Na_2SO_4 0,05M (80/20) solution. A polystyrene sulfonate standard was used for the calibration curve.

Raw material

Wet blue Spanish cattle hide shaved at 2.2 mm was used for this study. The but was cut in pieces of 10 x 15 cm. Hides were treated in a 300 mm-diameter, 150-mm wide laboratory drum, model Simplex-4 (Inoxvic), set at a rotation rate of 24 rpm. The test was performed in triplicate.

pH control and anionization

Bromocresol green indicators and universal indicator were used to control leather pH, and a cationic dye methylene blue solution was used to determine the degree of anionization. Bath pH was determined with a GLP 21 pH meter.

Products used

Two variables were used in this test: variable 1 for tests performed without amphoteric auxiliary, and variable 2 for tests performed with amphoteric auxiliary during the dyeing process. In variable 1, naphthalenesulfonic-free tests were used as a reference. In variable 2, an amine ethoxylated at 35% of active matter was used as amphoteric auxiliary (amine E), with amine-free tests used as a reference.

Dyes

Dyes Acid Brown 83 and Acid Black 210 were selected (see characteristics in Table I). The formula is shown in Table II (with % based on wet blue weight). Except for the dyes, the products were weighed in a 0.01 g precision laboratory scale. The products used in this process were commercially available products.

Evaluation of dyeing properties

In order to assess the dyeing properties of the different products used, dyeing intensity and levelness were measured with a Color Data Spectraflash SF-30 colorimeter. The same colorimeter was used to measure color levelness (ΔE* values: variation in total color) on ten points of the grain surface versus a reference point located in the center of the sample.

In order to control bath exhaustion, filter paper strips were impregnated with the different residual baths and allowed to dry. Colorimetric measurement of L* values was then performed.

L*=100 value indicates maximum luminosity, more white. L*=0 indicates minimum luminosity, more dark or more fixed dyestuff.

Table I

Characteristics of the dyes and the amine used

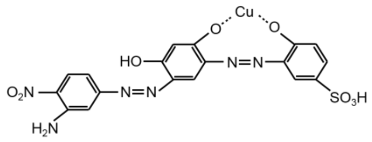
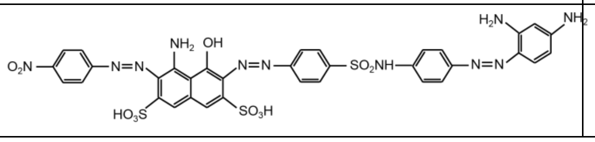
Name	Description	Structure	MW
Acid Brown 83	Cu-metallized diazo acid		557.5
Acid black 210	Triazo acid		861

Table II.

Procedure for the application of dyeing auxiliaries

PROCESS	OPERATION	OBSERVATIONS
Washing	200% Water at 35ºC, 0.2% Acetic acid, run 10 min.	

	0.2% Non-ionic surfactant, run 10 min, pH =3.2. Drain bath and wash 20 min.		
Neutralization Anionization	150% Water at 35ºC, 2% formate, run 30 min 0.2% Sodium bicarbonate, run 60 min, pH=4.4		Control of pH and degree of anionization in the leather.
	5% Naphthalenesulfonic, run 120 min, pH= 4.5-5.2. Drain bath and wash 10 min.		
Dyeing Fatliquoring	100% Water at 45ºC		Control of penetration and bath exhaustion.
	-	**2% amine E,** run 20 min	
	1.5% Acid Brown 83, **1.5% Acid Black 210,** run 60 min.		
	5% Sulfated neatsfoot oil 5% Sulfochlorinated fatty oil, run 60 min 1% Formic acid, run 60 min, pH= 3.8-4 Drain and wash 10 min.		

3. RESULTS AND DISCUSSION

Naphthalenesulfonic derivatives characterization

As previously mentioned, the purpose of this study was to assess the influence of each naphthalenesulfonic on penetration, levelness and intensity at the end of the dyeing process. The use of two chromatographic techniques allowed classifying naphthalenesulfonics according to their chain length and relative molecular weight.

RP-HPLC allows determining the degree of condensation of the polymers and qualitatively relating this degree to the chain length (n). This being a qualitative assessment, n values are mean and approximate values, and naphthalenesulfonics are classified according to their chromatographic profiles as long chain (n=12), medium chain (n=6) or short chain (n=2) products. Three chromatographic profiles according to time (minutes) and degree of condensation of the polymer are shown in Figure 1. Figures 1A and 1C correspond to the chromatographic profile obtained for the longest chain (NS1) and the shortest chain (NS6) product, respectively. Figure 1B shows the chromatogram of the medium chain products, that is, the remaining naphthalenesulfonics (NS2-NS5). These chromatographic profiles are similar during the first 50 minutes, where the first peak is obtained with the free monomer at a retention time of 20 minutes, followed by the dimer at 40 minutes, etc. These profiles start to differ as of 60 minutes, where the more condensed the polymer, the longer the chain. This is how naphthalenesulfonics are first classified (see Table III).

GPC allows studying the molecular weights of the polymers and the distribution thereof. Quantification is performed from calibration curves using polystyrene sulfonate as standard. Relative molecular weights calculated from time-related polymer concentrations are shown in Table III. These results are consistent with those obtained by RP-HPLC, where the longest chain product (NS1) has the highest molecular weight, the shortest chain product (NS6) has the lowest molecular weight, and the molecular weights of the remaining medium chain products lie between those two.

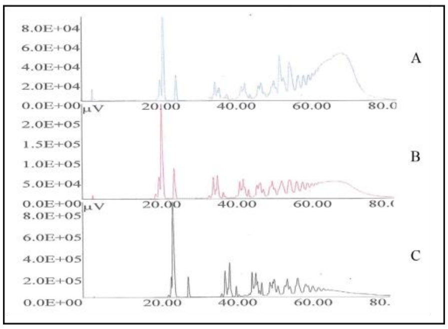


Figure 1. Chromatograms of three naphthalenesulfonics obtained by RP-HPLC. Three degrees of condensation: **A** long chain, **B** medium chain and **C** short chain.

Table III.
Naphthalenesulfonics characterization by RP-HPLC and GPC

Product	n	Relative molecular weight (Da)
NS1	Long	3.000
NS2	Medium	1.200
NS3	Medium	1.400
NS4	Medium	1.200
NS5	Medium	1.300
NS6	Short	600

Assessment of dyeing properties

In order to assess the dyeing properties of the studied products, two control points were marked in the process (Table II). Hide pH and anionization were controlled at the end of the process (after naphthalenesulfonic addition) and the values obtained were compared to the (naphthalenesulfonic-free) standard process. At the end of the dyeing/fatliquoring process (after amine addition), color intensity and degree of penetration of the dye mixture were assessed versus the amine-free reference process.

a) pH and anionization control

At the first control, leather pH was checked with two indicators (bromocresol green and universal indicator) and the degree of anionization and intensity was checked with methylene blue. Leather pH control showed pH values of 4.5-5 with the products and somewhat higher values (5.5-6) with the reference (see Figure 2(a)).

b) Anionization

Penetration control with methylene blue is shown in Figure 2(b). Methylene blue allows observing the degree of penetration of these products. This occurs thanks to the anionic element contained in naphthalenesulfonic acids — the SO_3^- reactive group —. This group reacts with the methylene blue cationic dye to yield a deep blue color. As shown in Table IV, product NS1 has the highest penetration (100%), followed by product NS3 (85%). The product-free reference has a null degree of anionization (0%). Therefore, the higher the molecular weight, the better the penetration of the product. Surface distribution on the grain side when using methylene blue is shown in Figure 2(c), and color intensity (L*) is shown in Table IV. The lowest L* value is obtained with NS1 (23.5, highest molecular weight) and the highest L* value (64.8) is obtained with the product-free reference. The values obtained show that intensity and molecular weight are closely related, that is, the higher the molecular weight, the higher the anionicity.

(a) (b) (c)

Figure 2. Leather cross sections after naphthalenesulfonic application. **(a)** Leather pH control with bromocresol green (left) and universal indicator (right). (**b**) Control of the degree of anionization of the naphthalenesulfonic with methylene blue. **(c)** Surface distribution on the grain side with methylene blue.

c) Penetration and dyeing intensity control

The second control with the two studied variables was performed upon the completion of the dyeing/fatliquoring process. This included penetration, intensity and levelness control without/with amine E in the substrate, and bath exhaustion control.

Dye penetration without and with amine E after cutting the hide strip is shown in Figure 3(a). The dye mixture shows color levelness in the penetration of both dyes (Acid Brown 83 and Acid Black 210).

The (higher relative molecular weight) NS1 product has the highest penetration in the two variables. The (naphthalenesulfonic-free) reference has the lowest penetration. Dye penetration is notably — and uniformly— increased by amine E. The comparison of product penetrations showed that the lower the molecular weight, the higher the influence of amine E. Dye penetration was proportional to anionicity penetration. Contrary to what was expected, the higher the molecular weight and the size of the chain, the better the penetration, both of the anionic part of the naphthalenesulfonic and of the dyes.

The naphthalenesulphonic derivative reduces the cationicity of the leather surface, thus making the product penetrate more easily. The higher the molecular weight, the higher amount of SO_3^- groups and cationicity of the leather is reduced to a greater extent. Figure 3(b) shows a schematic representation of this explanation.

Table IV

Control of the penetration and surface distribution of naphthalenesulfonics, and of dye penetration without / with amine E

Products	Control after adding naphthalenesulfonics		Control after adding dyes		
	Degree of anionization (%)	Surface distribution on grain side (L*)	Without amine E (%)	With amine E (%)	% Variation
NS1	100	23.5	100	100	0
NS2	70	31.4	75	80	6
NS3	85	27.0	84	92	10
NS4	60	32.8	75	89	18
NS5	60	37.3	78	90	15
NS6	50	37.4	65	88	35
Reference	0	64.8	45	55	22

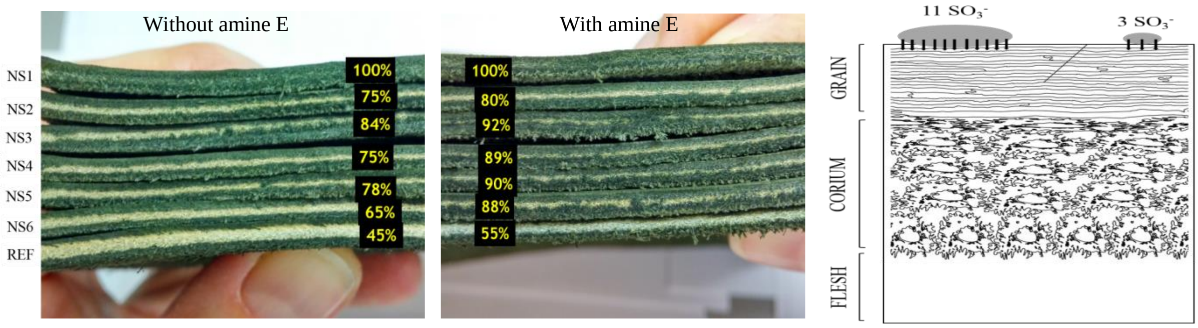


Figure 3. (a) Penetration control of dyes without amine E (left) and with amine E (right). **(b)** Representation of the physical effect of naphthalenesulfonics on the hide surface.

Color intensity (L*) on the grain surface is shown in Table V. The reference has the highest color intensity (lowest L*), followed by NS6 (lowest molecular weight), in both variables. Dyeing intensity is increased by adding amine E in the products with higher molecular weights (NS1, NS2, NS3).

d) Color levelness control

Color levelness values were obtained by measurements performed on ten points of each sample. The higher the ΔE* values, the poorer the levelness. The values obtained for each product in the two variables are shown in Table V. Color levelness gets poorer with decreasing molecular weights in the variable without amine E. In this variable, ΔE* values show little variation between molecular weights —from 3.000 (NS1) to 1.200 (NS2 and NS3) — with a sudden fall to molecular weight 600 (NS6) and much lower in the (product-free) reference. The addition of amine E improved the levelness values of all products (variation %), more significantly so with decreasing molecular weights, and to a higher proportion as compared to the product-free variable (reference).

Table V
Color intensity and levelness values, with and without amine E

Product	Color intensity			Color levelness		
	Without amine E (L*)	With amine E (L*)	Variation (%)	ΔE* without amine E	ΔE* with amine E	Variation (%)
NS1	31.3	26.4	15.6	3.8	3.6	5.2
NS2	31.1	29.4	5.4	4.2	3.8	9.5
NS3	30.8	26.2	14.9	4.3	3.7	13.9
NS4	30.3	30.6	-0.9	4.3	3.6	16.2
NS5	31.0	31.1	-0.3	4.4	3.6	18.2
NS6	27.9	27.4	1.7	7.0	4.0	42.8
Reference	21.3	21.7	-1.8	12.5	6.2	50.4

e) Bath exhaustion

Finally, the values obtained for dyeing exhaustion from baths are shown in Table VI. In the variable without amine E maximum exhaustion was obtained with the reference (L*=84.2) and minimum exhaustion was obtained with NS1 (maximum molecular weight). The rest of products showed similar exhaustions, or exhaustions with minor variations. In the variable with amine E maximum exhaustion was also obtained with the reference, and exhaustions unrelated to molecular weight were obtained with the rest of products. The addition of amine E increased dye exhaustion in all cases (by 15-17%). Exhaustion variation (influence of amine E) was maximum with NS1 (maximum molecular weight) and minimum with the reference.

Table VI.
Bath exhaustion quantitative assessment

Product	(L*) Exhaustion without amine E	(L*) Exhaustion with amine E	Variation (%)
NS1	44.3	58.6	30.9
NS2	57.1	67.6	18.3
NS3	50.2	58.0	16.7
NS4	53.6	60.7	13.2
NS5	49.8	58.7	17.8
NS6	52.4	64.9	23.8
Reference	84.2	85.0	1,0

4. Conclusion

Six naphthalenesulfonic acid derivatives were characterized with two chromatographic techniques: RP-HPLC and GPC. RP-HPLC allows qualitative determination of polymer chain length according to their degree of condensation. For its part, GPC is highly suitable to ascertain the distribution of polymer molecular weights. The application of these two techniques allowed determining the structure of naphthalenesulfonics and thus relating their structure to the physical-chemical properties observed in the application process.

In naphthalenesulfonic derivatives applied as neutralization auxiliaries, the higher the molecular weight and the number of sulfonic products, the better their penetration and the penetration of the dye mixture. While color levelness is increased with increasing molecular weights, bath exhaustion is decreased with increasing molecular weights.

Non-ionic amine E is an excellent dyeing auxiliary that improves both the penetration and the levelness of the dyes. Color intensity is notably improved in the products with higher molecular weight. Finally, the addition of non-ionic amine improves exhaustion of all variables.

5. ACKNOWLEDGMENTS

The authors would like to thank to the Leather Application Laboratory, Department of Analysis and Department of R&D of Cromogenia Units, S.A.

6. REFERENCES

1. Morera, J M, Química Técnica de Curtición, Escola univ. d’enginyeria, 2003, pp 123.
2. Soler, J, Procesos de curtición, UPC, 2000, pp 177-200.
3. Heidemann, E, Fundamentals of leather manufacturing, Roether, 1993, pp 445.
4. Portabella, M, Tecnología química del cuero, 1962, pp 226.
5. Palop, R, Parareda, J, Ballús, O, Estudio aplicativo de los recurtientes sintéticos. Parte I, AQEIC, **1**, 2008.
6. Ballús, O, Palop, R., Influencia de la aplicación de un recurtiente anfótero en las propiedades del cuero, Parte I. 63º Congreso AQEIC, Igualada 2014.
7. Ballús, O, Palop, R., Influencia de la recurtición con sintanes en la tintura del cuero, 62º Congreso AQEIC, Lorca 2013.
8. Covington, A, Tanning Chemistry. The science of leather, RSC Publishing, 2009, pp 385-387.
9. Adzet J M, Química técnica de tenería, Escuela de Tenería de Igualada, 1985, pp 432-433.

SURFACE AREA GAIN OF LEATHERS DRIED UNDER DIFFERENT CONDITIONS

Huseyin Ata KARAVANA*, Kemal KILINC

Abant Izzet Baysal University Gerede Vocational School Textile, Footwear and Leather Department, 14900, Gerede, Bolu, TURKEY
Ege University Engineering Faculty Leather Engineering Department, 35100, Bornova, Izmir, TURKEY
Email address: huseyin.ata.karavana@ege.edu.tr

Drying is one of the most important leather production processes which is necessary to obtain usable leather form from skin and determines the basic structural, chemical and physical properties of the leather. Using different drying methods in the footwear upper production affect the change in surface area of the leathers as distinct from each other. Surface area gain has a great significance since the footwear upper leathers are sold depend their size of the surface area. In this research, it is determined that the surface area gain of the each footwear upper leathers which manufactured using the wet-toggle and vacuum drying methods that are different drying processes, and the area gain of the leathers are compared. As a result, it is observed that the significance changes occurred on the surface area gain of the same origin upper leathers as using the different drying methods and conditions. Especially, the wet-toggle for the drying of footwear upper leathers is a preferable drying method because of the better surface area gain provided by the method.

Keywords: Shoe upper leather, wet-toggle drying, vacuum drying, area gain

1. INTRODUCTION

Different properties and fastness are expected from the finished leathers according to the utilization areas of the products. The drying process has a big contribution, besides to the chemicals used for the leather having these properties and fastness. The physical properties such as final structure, softness and elasticity are basically formed as the result of the drying process.

In addition to desired physical properties, one of the most important factors is surface area gain for the leather producer. Since the price of finished leathers is determined by the surface area size. Leather production is a subject of commerce, so that gaining or retaining of the leather surface area is had to handle as a very important concept. For this reason, most of the drying methods have character increasing the surface area efficiency. Therefore, investigation of the effects of different drying methods selected for leather drying and the variables of drying processes on leather surface area efficiency is one of the very important research topics. Different drying methods are used for drying of the upper leather like other leather types. Vacuum drying method is the most favourite drying method for upper leather. In recent years, wet-toggle drying method have been widely used since it provides features such as desired softness, handle and drum milling effect and provide a high surface area gain for the leather.

The effects of hang drying, wet toggle drying and vacuum drying methods on surface area gain of upper leathers were comparatively determined in this study.

2. MATERIAL AND METHOD

2.1. Material

In this research, eighteen sides of wet-blue leathers for upper leather production originates from Azerbaijani were used as material.

2.2. Method

Wet-blue side leathers were subjected to dyeing, retanning and fatliquoring processes with a recipe suitable for standard upper leather treatment. Then, they were setting out after being horsed-up for one night before drying.

2.2.1. Drying Process

After setting-out process, the eighteen side willows were divided into three groups for applying different drying methods. Drying methods and conditions applied to the leathers are given below.

Hang drying: The drying hanger unit with the 600 meters total length and 2 m/min speed was used. The temperature of closed drying cabin unit with 40 meters length where placed at the end of hanger unit was adjusted at 70°C.

Wet-toggle drying: The temperature of the wet-toggle drying cabin used in the study was adjusted at 60°C and drying was applied for four hours.

Vacuum drying: The temperature of the vacuum drying unit used in the study was adjusted to 50°C, and four different drying durations that are 50, 100, 200, 400 seconds were applied.

Drying process was completely terminated when the moisture level of the leathers reached 12 % for all drying trials.

Dried side willows were subjected to staking, drum milling for three hours and staking processes, respectively.

2.2.2. Area Measurement

The surface areas of wet-blue side leathers, side willows that were staked after the drying process and drum milled after the staking process and staked after the drum milling process were measured by using a surface measuring machine in order to determine the changes in the surface areas of side willows by drying and mechanical processes after drying.

3. RESULTS AND DISCUSSION

The surface area of leathers is main topic for leather commerce. It is strongly influenced by drying, stretching, storage conditions and any kind of heating in the dried state (Heidemann, 1993).
Generally, leather is sold based on surface area and maximizing of surface area yield is the aim of leather commerce. This goal does not decrease quality of leathers (Manich et al., 2006).

The most common problem involved in the leather drying process is shrinkage. This problem is mostly valid in leather tanned with metal ions, including chromium. Leather shrinks during drying process like other hydrophilic materials. Surface area yield decreases by shrinkage. The shrinkage of hydrophilic materials after removal of water is well-known behaviour. During water removal, voids filled with water which is reduced by the influence of the internal pressure slowly tightening. Therefore the material shrinks (Liu and Dimaio, 2000).

Although a little surface area could be gain by mechanical operations like sammying and setting out, this case could be lost in the progressive stages. More persistent surface area gain is provided by drying process which leather is stretched like toggled drying. Significantly surface area gain could be obtained by biaxial stretching of leather (Leather International, 2006).

When drying is made without stretching, elastic strain would be loose. Surface area decreases accordingly elasticity of leather significantly increase (Bienkiewicz, 1983).

Surface area measurement values are given in Table 1.

Table 1. Surface area measurement values of leathers (dm^2).

Drying Methods	**n**		**Wet-Blue**	**Staking**	**Drum Milling**	**Drum Milling + Staking**
Hang Drying	3	Min.	68,00	68,00	68,00	68,00
		Max.	100,00	101,00	101,00	103,00
		X±S.E.	86,00±9,45	87,00±9,85	87,00±9,85	88,00±10,41
Wet-Toggle Drying	3	Min.	74,00	89,00	85,00	86,00
		Max.	98,00	122,00	120,00	121,00
		X±S.E.	83,33±7,42	102,67±9,94	99,67±10,49	101,00±10,41
Vacuum Drying 50 °C 50 s	3	Min.	68,00	72,00	70,00	72,00
		Max.	100,00	103,00	103,00	104,00
		X±S.E.	85,33±9,33	87,33±8,95	86,00±9,54	87,67±9,24
Vacuum Drying 50 °C 100 s	3	Min.	81,00	82,00	81,00	83,00
		Max.	97,00	98,00	97,00	98,00
		X±S.E.	90,67±4,91	92,00±5,03	91,00±5,03	92,67±4,84
Vacuum Drying 50 °C 200 s	3	Min.	90,00	92,00	90,00	91,00
		Max.	102,00	108,00	106,00	107,00
		X±S.E.	97,33±3,71	100,67±4,67	99,00±4,73	100,33±4,81
Vacuum Drying 50 °C 400 s	3	Min.	75,00	79,00	78,00	79,00
		Max.	90,00	92,00	91,00	92,00
		X±S.E.	83,67±4,48	87,00±4,04	85,67±3,93	87,00±4,04

Surface area measurement values of leathers after staking process are higher than the surface area measurement values of wet-blue leathers in all drying methods and conditions (Table 1). It can be said that, the surface areas of the leathers dried by using different drying methods and conditions were showed increase according to their surface area in wet-blue stage (Figure 1).

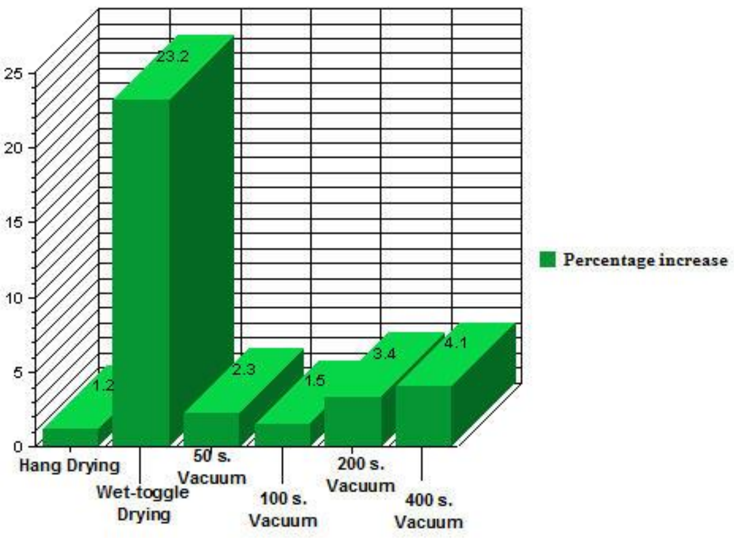


Figure 1. Percentage increase according to surface area measurements of wet-blue.

Generally, the area retention of leather increases steadily with the increase of drying period. Because, the longer drying period causes to remain less water in the leather and the lower residual water content enables higher area retention. Decreasing the initial water content to a certain level, this tendency steadily becomes reverse. With the increase of the drying period, this behaviour much more revealed. Probably, the leather is too dry and loses the elongation ability during toggled drying lead to lower area retention (Liu et al., 2002a).

After staking process, the leather usually goes to the drum milling process for increasing the softness of the leather. Drum milling is a physical softening process in which leather is tumbled in a dry drum fitted with wood dowels with atomized moisture injected into the tumbler. Desired softness can be generally obtained by carefully control of the drum speed, period and humidity inside the drum (Liu et al., 2011).

The cost of labour is low in the drum milling process and a more effective softness can be achieved than the other staking methods. There is no negative effect of drum milling on the strength of the leather, but the surface area loss is between 3-6%. Decrease of the surface area in the first four hours is highest (Toptaş, 1993).

It is seen that drum milling process applied after staking process is shown to reduce the surface area of leathers in all drying methods except hang drying method (Figure 2).

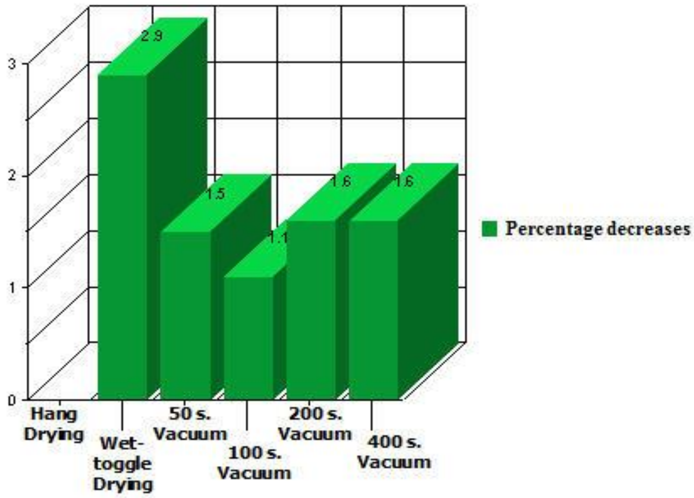


Figure 2. Percentage decrease of the surface area after drum milling.

Liu et al. (2011) investigated that the effects of conditioning, staking and drum milling processes on the retention of surface area gained by toggling process. The results indicated that toggling has markedly effect on surface area retention, conditioning and staking have a little effect on area retention, whereas the drum milling significantly decreased the surface area.

It is observed that the tendency of decreasing on surface area after drum milling is also higher in the drying methods which provide higher surface area gain after staking process. Despite this decrease, it is also seen that the surface areas after drum milling in all the drying methods are higher than the surface areas of wet-blue leathers.

According to the measurement values of the leathers after drum milling, the surface areas of the leathers were increased after the staking process (Figure 3).

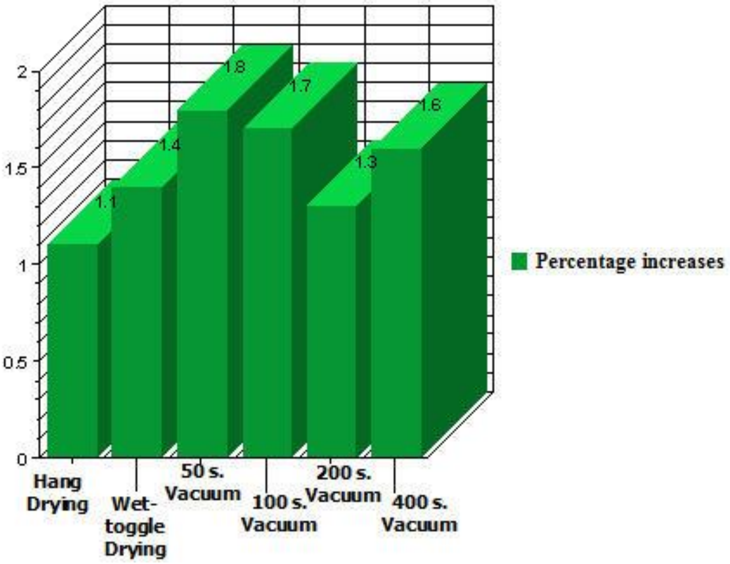


Figure 3. Percentage increase of the surface area after staking process applied after drum milling.

It is commonly known that the drying process often causes the leather fibers to stick together. Mechanical action from staking is necessary to break the weak adhesion within the fiber structure, thereby promoting fiber mobility (Liu et al., 2002b).

4. CONCLUSION

Surface area of the leathers has been increased in all drying methods compared to the wet-blue status. The maximum surface area gain was observed in the leathers that are subjected to wet-toggle drying method. This was followed by vacuum drying processes. The leathers that were subjected to the hang drying have been minimum surface area gain. The longest period vacuum drying process achieved maximum surface area gain. The drum milling process hasn’t caused any changes in the surface area of hang dried leathers, but has caused decrease in the surface area of leather in all other drying processes. Maximum reduction in the surface area was seen in the leathers dried by the wet-toggle drying method. It is understood that the surface area reduction after drum milling is also higher in the drying methods which provide high surface area efficiency.

Adding staking after drum milling provided surface area gain of the leathers for all drying methods. It is determined that staking process clearly helps to increase surface area yield of the leathers.

5. ACKNOWLEDGEMENT

The authors would like to acknowledge 2005 DPT 001 project and Ege University Engineering Faculty Leather Engineering Department for enabling us to use its laboratory instruments.

6. REFERENCES

1. Bienkiewicz K. *Physical Chemistry of Leather Making;* Robert E. Krieger Publishing Company, Malabar, Florida, 1983, pp. 510-520.
2. Heidemann E. *Fundemantals of Leather Manufacture;* Eduard Roether KG Druckerei und Verlag, Darmstadt, 1993, pp. 542-567.
3. Leather International Magazine, Effect of Mechanical Stretching on Area Yield and Quality. http://www.leathermag.com/features/featureeffect-of-mechanical-stretching-on-area-yield-and-quality/, (Accessed date: 2 Ekim 2016)
4. Liu C K, DiMaio G L, Vacuum Drying Studies for Leather. *JALCA,* 2000, **95**, 102-110.
5. Liu C K, Latona N P, DiaMio G L, Area Retention Studies for Vacuum-Dried Leather. *JALCA,* 2002a, **97**, 355-368.
6. Liu C K, Latona N P, DiaMio G L, Staking and its Interaction with Fatliquoring on Vacuum-Dried Leather. *JALCA,* 2002b, **97**, 329-338.
7. Liu C K, Latona N P, Lee J, Drying Leather with Vacuum and Toggling Sequentially. *JALCA,* 2011, **106**, 76-82.
8. Manich A M, Castellar M D, Gonzales B, Ussman M H, Marsal A, Influence of Leather Stretching to Gain Area Yield on Its Stress-Relaxation Behavior. *Journal of Applied Polymer Science,* 2006, **102**, 6000-6008.
9. Toptaş A. *Deri Teknolojisi*; Sade Ofset, İstanbul, 1993, pp. 445-475.

ACSIL O-06

WASTE TO WEALTH APPROACH: ADHESIVE FROM THE UNUSED GOAT HEAD SKIN

Md. Abul Hashem*, Md. Shahruk Nur-A-Tomal, Md. Hasibur Rahman Sheikh, Syeda Anika Bushra

Department of Leather Engineering, Khulna University of Engineering & Technology (KUET), Khulna-9203, Bangladesh, Tel.: +88 041 769468-75 Ex-753,
E-mail: mahashem96@yahoo.com, mahashem@le.kuet.ac.bd

Slaughterhouse byproduct management is an important issue for the green environment. The byproduct from the slaughterhouse e.g. cow, buffalo, goat and sheep skin is the basic raw materials for the tanning industry. After slaughtering cow and buffalo head skin is used in small scale for leather processing. But in the case of goat and sheep, the head skins are disposed away without any proper management to the environment from where gaseous air pollutants are continuously merged to the atmosphere. In this study, an investigation was carried out for the adhesive production for commercial use from the unused goat head skin by means of a cleaner environment. Goat head skin was collected from the local slaughterhouse: soaked and heat treated to extract the collagen in soluble phase. The extracted solution was dried and obtained adhesive was investigated for commercial application. The produced adhesive could be used in the packaging industry, furniture, plumbing, shoe making, book binding, etc. Adhesive was prepared from the goat head skin by using the simple and easy technique with a few chemical. It was estimated that Bangladesh could produce 625 MT adhesive per year only from the unused goat head skin.
Keywords: Goat head skin, Adhesive, Environment, Pollutant.

1. INTRODUCTION

The increasing growth of population is rising food demand. Meat is one of most good nutritious foods which is obtained by slaughtering animal e.g., goat, sheep, cow, buffalo, etc. In the last three decades globally meat production was double (Mekonnen and Hoekstra, 2012); it has been anticipated a steady doubling growth of meat production until 2050 (Bouwman et al. (2013). Slaughterhouse is most common in every country where along with meat a large amount of wastewater and solid wastes e.g., raw hide/skin, trimmings, blood, dung, hair, etc. are generated.

Slaughterhouse byproduct management is an important issue for the green environment. The byproduct from slaughterhouse e.g., cow, buffalo, goat and sheep skin is the basic raw material for the tanning industry. After slaughtering cow and buffalo head skin is used in small scale for leather processing. But in the case of goat and sheep, the head skins are disposed away without any proper management to the environment.

The skin is mostly proteinaceous substances, which are hydrolyzed to amino acids by proteolytic bacteria; amino acids are further hydrolyzed by bacteria and liberate NH_3, H_2 and CO_2 (Ref). The skin also contains some extend fatty substances which are hydrolyzed by bacteria and cause volatile fatty acids emission (Hashem et al. 2015). Individuals frequently inhale the liberated gases and suffer in difficulties. The emitted gases are continuously merged to the air, which causes atmosphere pollution. The residue of skin remained after degradation also has a diverse effect on soil and aquatic life. In the rainy season, the dumped skins are washed away to low lying area and finally fall into the river, which causes aquatic imbalance. Solid waste disposal is increasingly becoming a huge challenge due to strict environmental legislations worldwide. The management of slaughterhouse by-product is an important issue for the cleaner environment.

Animal skin contains 29.0% collagen (Sharphouse 1971). As the animal skins are collagenous materials, the raw goat head skin could be a great source for the adhesive production. Adhesives are capable of holding substances together by surface attachment. In our daily life, adhesives are used for various purposes e.g., packaging industries, furniture, shoes, books, etc.

In Bangladesh, every year 30 million pieces of goats are slaughtered for meat purpose (Aziz 2012). The huge number of unused goat head skin can be converted to adhesive production that will help to keep the environment pollution free. In this study, an investigation was made to produce adhesive for commercial use from the unused goat head skin by means cleaner production.

2. MATERIAL AND METHODS

2.1 Sample collection

Twenty (20) pieces raw goat head skins were collected from the local slaughterhouse Khulna, Bangladesh as free of cost. The collected goat head skins were washed with wetting to remove blood, dirt, etc., and unwanted parts were removed. The clean goat head skins were cut into small pieces to facilitate the further operations.

2.2 Reagents

Commercial lime and wetting agent were collected from a tannery at Khulna, Bangladesh.

2.3 Adhesive extraction from goat head skin

The scheme for the preparation of adhesive from the unused goat head skin is shown in Figure 1.

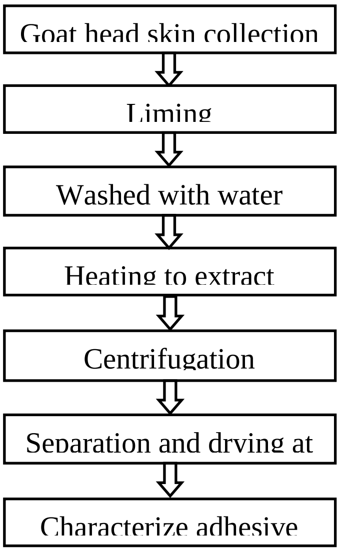


Figure 1: Scheme for the preparation of adhesive from goat head skin

In liming of raw goat head skin, about 30 g sample was treated with 3% lime for 48 h. Then, the limed skin was repeatedly washed with water to remove lime. The lime treated goat skin was heated in a water bath for several hours to extract adhesive from the skin into the aqueous phase. The extracted aqueous phase adhesive was centrifuged at 3000 rpm for 20 min. The supernatant of the mixture was separated and dried in an oven at 60°C for removal of moisture.

2.4 Optimization of adhesive extraction

Assays were carried out to optimize the extraction process by varying the parameters such as extraction temperature, extraction time and frequency of extraction so that higher amount of adhesive could be attained in a large scale production. The optimized conditions were established by investigating the amount of extracted adhesive.

To determine the optimal extraction time for adhesive extraction from the head goat skin, the samples was allowed to heat for 2, 4, 6, 8, and 10 h respectively, while the other parameter time (6 h) remained constant. Different temperatures 60°C, 70°C, 80°C, and 90°C were investigated to extract the maximum amount of adhesive from the goat head skin. To optimize the frequency of extractions, the extraction process was repeated for 3 times.

2.6 Characterization of the prepared adhesive

The properties of adhesive were detected. The adhesive bond strength of the prepared adhesive was determined by T-peel strength tests of leather-to-leather joining following the standard EN 1392:2007. The leather strips were cut into 20 × 100 mm size. The leather surface was roughed using a roughing machine. The adhesive was applied to 20 × 80 mm surfaces of leather strip using a metering rod to ensure adhesive film thickness. The leather strips were joined under a pressure and it was left to dry in the open air. The T-peel strength was measured using an Instron 1011 Universal Testing Machine (Instron Ltd, UK).

3. RESULTS AND DISCUSSION

3.1 Effect of time

The effect of time to extract adhesive from the goat head skin is depicted in Figure 2.

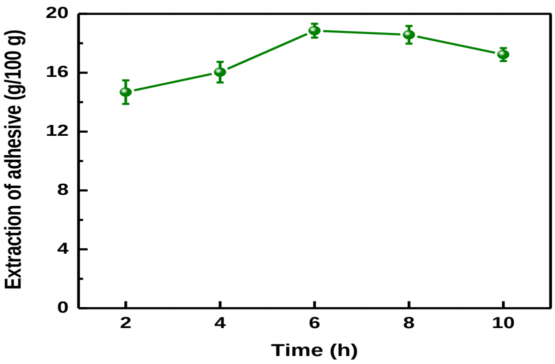


Figure 2: Effect of time to extract adhesive from goat head skin

It is clear that with increasing temperature, amount of adhesive extraction was increased. During experimentation, it was observed that the amount of adhesive was increased significantly in the initial stages while increasing time and subsequently, the amount of adhesive was decreased with increasing the time. In the case of the less time period, the amount of adhesive was unsatisfactory. In longer time duration, it is supposed that greater collagen breakdown had occurred. At 60°C, adhesive extraction was 9 g per 100 g skin but at 70°C adhesive extraction was 11 g per 100 g skin. Therefore, 6 h was selected to be the optimal time to extract adhesive in this experiment.

3.2 Effect of temperature

In Figure 3 shows, the effect of temperature to extract adhesive from the goat head skin. It is clear that with increasing the temperature the amount of adhesive extraction was increased. At 60°C adhesive extraction was 9 g per 100 g skin but at 70°C adhesive extraction was 11 g per 100 g skin. It seems that temperature at 90°C adhesive extraction was twice than adhesive was extracted at the temperature 60°C. It is obvious that collagen protein breakdown above 80°C, therefore, higher the temperature more adhesive was extracted at temperature 90°C (18.9 g adhesive/100 g goat head skin). Based on the experimental result, 90°C was selected as the optimal extraction temperature.

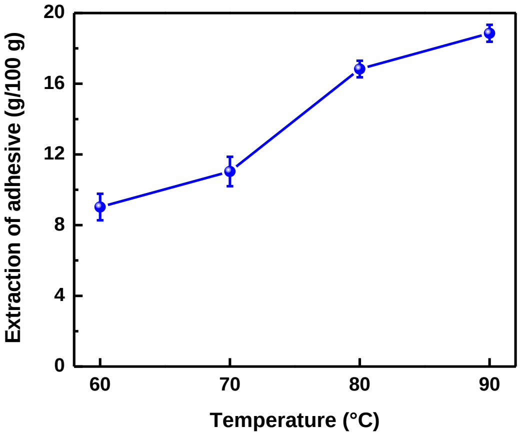


Figure 3: Effect of temperature to extract adhesive from goat head skin

3.3 Frequency of adhesive extraction

Adhesive from the goat head skin was extracted at different frequencies. In Figure 4 shows that at the optimized temperature (90°C) after first 6 h 18.9 g adhesive was extracted per 100 g goat head skin.

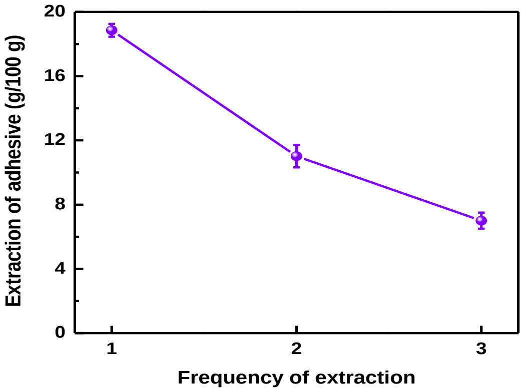


Figure 4: Effect of number of extraction to extract adhesive from goat head skin

From the same goat head skin after 12 h and 18 h adhesives were extracted 11.0 g and 7.0 g per 100 g goat head skin. It is clear from the above Figure 4 that maximum three times adhesive extraction could be done from the goat head skin. By extracting three times 36.9 g adhesive could be obtained from each 100 g goat head skin.

3.4 Efficiency of the proposed process

In Bangladesh, every year 30 million goats are slaughtered for the meat production (Aziz 2012). It was estimated that 3314 MT raw goat head skin are thrown away without producing any byproduct. Yearly 625 MT adhesive could be extracted from the unused goat head skin to make as a valuable product for using in our daily life. The disposed goat head skin makes the environment pollute. Proper management could be a better option to save the environment.

3.5 Characteristics of the adhesive

The adhesive was brownish red in color. The peel strength of grain-to-flesh and grain-to-grain leather joining was 8.33 N/cm and 6.86 N/cm respectively. The results reveal that the adhesive prepared from the unused goat head skin has binding properties. The bond formed by joining two substances is shown in Figure 5.


(a) (b)

Figure 5: Bond formed by prepared adhesive (a) grain-to-flesh and (b) grain-to-grain

4. Conclusions

In Bangladesh, all the goat head skins are disposed of without utilization, which is causing environmental pollution. The present study was carried out to produce adhesive for commercial use from the unused goat head skin by means of a cleaner environment. The glue was extracted from the goat head skin using simple heat. In Bangladesh, yearly 625 MT adhesive could be extracted from the goat head skin, which could be used in our daily life. The proper management process of the unused goat head skin could to save the environment from pollution as well as produce valuable end product.

5. References

1. Mekonnen M M, Hoekstra AY, A global assessment of the water footprint of farm animal products. Ecosystems. 2012, **15**, 401-415.
2. Bouwman L, Goldewijk K K, Van Der Hoek K W, Beusen A H W, Van Vuuren D P, Willems J, Rufino M C, Stehfest E, Exploring global changes in nitrogen and phosphorus cycles in agriculture induced by livestock production over the 1900-2050 period. Proc. Natl. Acad. Sci. USA. 2013, **110**, 20882-20887
3. Hashem M A, Nur-A-Tomal M S, Mondal B K, Generation of fleshings at beamhouse in tannery and its environmental impact assessment: Bangladesh perspective. Bangladesh J. Sci. Ind. Res. 2015, **50**, 227-232.

FABRICATION OF ANTIBACTERIAL CASEIN-BASED ZNO NANOCOMPOSITE FOR LEATHER FINISHES THROUGH IN-SITU ROUTE

Wang Yanan*, Ma Jianzhong, Xu Qunna, Qianqian Fan

College of Bioresources Chemical and Materials Engineering, Shaanxi University of Science & Technology, Xi'an, 710021, China

E-mail:704113065@qq.com, majz@sust.edu.cn, xxqqnn870304@163.com, fqleather@163.com

Casein, a natural polymer extracted from raw milk, has superior film-forming properties including excellent adhesive force and strong heat resistance. Nevertheless casein film is easily spoiled by bacteria attack, which might restrict its practical applications. In this paper, casein-based ZnO nanocomposite leather finishing material was fabricated through in-situ polymerization aim at improving the antibacterial activity of casein films. The structure and size of nanocomposite were characterized. The water absorption of the films was also detected. DLS measurement results showed that the size of nanocomposite latex particles was 249-459 nm. Moreover, the composite film displayed superior mechanical property, high water resistance and excellent antibacterial activity against S. aureus and E. coli. This work provides a feasible pathway for fabricating natural polymer-based nanocomposite antibacterial films which will has great potential use in some fields.
Keywords: casein; ZnO; in-situ polymerization; antibacterial; leather finishes

1. INTRODUCTION

Bionanocomposite, a new generation of composite materials, has attracted great interests in the frontier of materials science, life science and nanotechnology. Bionanocomposites are composed of a natural polymer matrix and organic/inorganic filler with at least one dimension on the nanoscale (Shafei et al. 2011). These bionanocomposites show remarkable advantages of biodegradability and biocompatibility in tissue engineering, drug release, biosensor, photoelectricity, coating and packaging applications.

Casein, a natural polymer precipitated from raw milk by acidification, is a promising polymer matrix for controlled drug delivery, leather finishing, water-based ink and food packaging. In addition to its biodegradability and biocompatibility, casein exhibits good film-forming property, such as excellent adhesive force and strong heat resistance. Nevertheless, casein-based films often has less flexibility, water resistance and tends to be easily spoiled by bacteria attack, which might restrict its practical applications. In our previous research, SiO_2 (Ma et al. 2013), and TiO_2 (Xu et al. 2015) nanoparticles were introduced into casein matrix separately to obtain casein-based SiO_2/ TiO_2 nanocomposite, thus endowing the composite with high-gloss, flexibility or self-cleaning property. To obtain antibacterial casein-based nanocomposite, ZnO nanoparticles (ZnO NPs) were introduced into casein matrix via in-situ conversion in the presence of precursor zinc acetate. Highlights of this method lies in the facile fabrication process and less demand of organic solvent. Moreover, biodegradable and biocompatible polymer matrix could stabilize the nanoparticles and better control the morphology and particle size via in-situ formation (Mujeeb et al. 2015). The as-prepared film harbors excellent antibacterial activity, superior tensile strength and well flexibility, which can be applied as film-forming agent for leather finishing.

2. EXPERIMENT AND METHODS

2.1 Materials

Casein (CA) was purchased from Fonterra Co-operative Group Ltd. Caprolactam (CPL) and ammonia were supplied by Tianjin Hongyan Reagent Factory. Triethanolamine (TEA) was obtained from Tianjin Tianli Chemical Co, Ltd. Zinc acetate dehydrate was purchased from Tianjin Kemiou Chemical Reagent Co, Ltd. All the reagents were analytical grade and used without further purification.

2.2 Preparation of casein-based ZnO nanocomposite (CA-CPL/ZnO nanocomposite)

Various concentrations（0%, 1%, 1.5%, 2%, 2.5%）of ZnO precursor were introduced to prepare casein-based ZnO nanocomposite. Firstly, 10g of casein were added to TEA aqueous solution with constant stirring at 65°C for 2 h. When casein was completely dissolved, the temperature was raised to 75°C, CPL aqueous solution and silane coupling agent were drop-wise added into the system separately with suitable dropping speed allowing reacting for another 1h. Then pH of the system was adjusted to an appropriate value with ammonium liquor. Zinc acetate solution was drop-wise added into the system to prepare antibacterial casein-based ZnO nanocomposite.

2.3 Characterization and application

Characterizations. DLS (dynamic laser scattering) measurement of casein-based ZnO nanocomposite was determined by using NANO-ZS90 (Malvern, Britain), each specimen was repeated in duplicate. FT-IR spectra of CC and CCZ4 films were recorded from 400 to 4000 cm^{-1} using TG-IR-GC instrument (STA449 F3/VERTEX 70/Agilent 5977A, Bruker/NETZSCH/Agilent).

Water absorption rate. Each film was cut into 2 square centimeters. Before testing, all of films were firstly air-dried at 25°C and then vacuum-dried at 60°C until constant weight (W_1) was obtained. The latex films were immersed into deionized water at 25°C for 24 h. Then the latex films were taken out and immediately weighted (W_2) after wiping out the surface water. Each specimen was repeated in duplicate. The water absorption was calculated using the following formula:

$$\text{Water absorption} = \frac{W_1 - W_2}{W_1}$$

Antibacterial activity. The Halo Test method was performed using agar culture-medium. Filter papers immersed by CA-CPL/ZnO emulsions were cut into 20mm circular slices. Then the slices were attached to S. aureus-cultured agar and E. coli-cultured agar plates. After that the prepared culture were incubated at 37°C for 48 h. A bacterial inhibition zone was formed around the film. The diameter of the inhibition zone (W_{inh}) was calculated using the following equation:

$$W_{inh} = \frac{d_1 - d_2}{2}$$

where d_1 is the total diameter of the inhibition zone, d_2 is the diameter of the film (20 mm).

Leather Finishing Application. Casein-based ZnO nanocomposites were applied in leather finishing experiments with CA-CPL as the reference. The tensile testing, vapor permeability and water-vapor permeability of the finished leather was studied according to the procedure detailed in reference (Ding et al. 2015).

3. RESULTS AND DISCUSSION

3.1 Size distribution of CA-CPL/ZnO nanocomposite

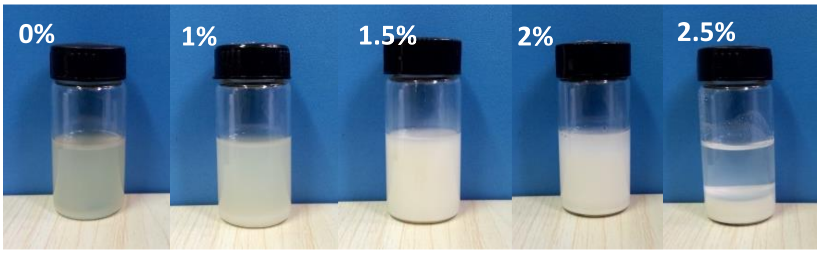


Fig.1 CA-CPL/ZnO nanocomposite emulsion with different ZnO precursor dosages

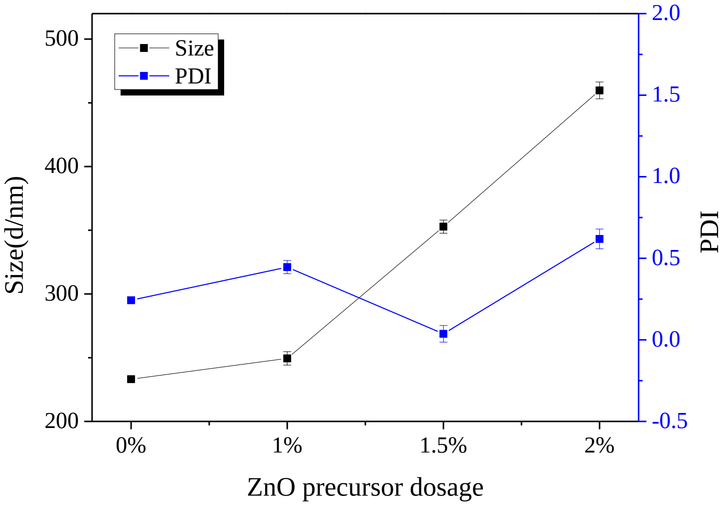


Fig.2 Particle size and PDI of CA-CPL/ZnO nanocomposite against precursor fraction

Fig.1 shows the appearance of CA-CPL/ZnO emulsion. After the generation of ZnO nanoparticles, CA-CPL/ZnO emulsion became milk white from yellowish green. When the dosage of precursor was increased to 2.5 %, delamination of CA-CPL/ZnO occurred. The particle size and size distribution of CA-CPL/ZnO were also shown in Fig.2. It can be seen that the average size of CA-CPL is smaller than that of CA-CPL/ZnO. More interestingly, the average size of CA-CPL/ZnO was increased as ZnO dosage increases, which might due to agglomerates of ZnO nanoparticles and ZnO crystal growth. The PDI of all samples was less than 0.7. It also shows that there was a uniform dispersion for CA-CPL/ZnO nanocomposite with precursor dosage range from 0% to 2%.

3.2 FT-IR

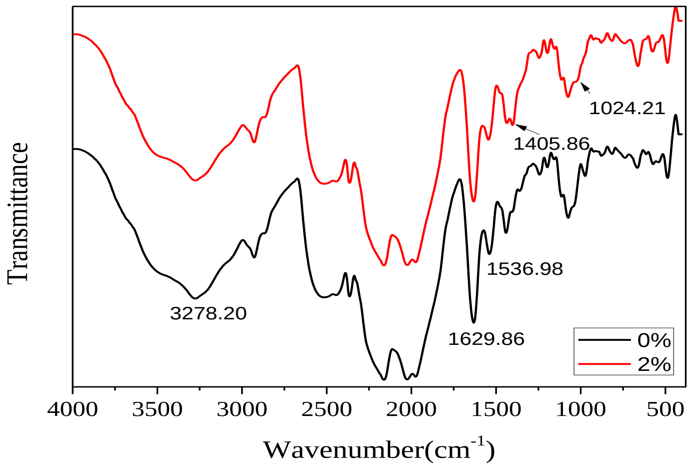


Fig.3 FT-IR spectra of CA-CPL/ZnO nanocomposite with different precursor dosages, a) 0%; b) 2%

Fig.3 showed FTIR spectra of CA-CPL and CA-CPL/ZnO composite. The characteristic absorption peaks of CA-CPL at 3278.20 cm^{-1}, 1629.86 cm^{-1} and 1536.98 cm^{-1} could be attributed to the stretching vibration of N-H, stretching vibration of –C═O and stretching vibration of the C-N, respectively cho et al. 2014). CA-CPL/ZnO composite showed the similar characteristic peaks at 3276.98 cm^{-1}, 1627.78 cm^{-1} and 1541.51 cm^{-1}, while a new and weak absorption peak around 1405.86 cm^{-1} was observed in the spectrum of CA-CPL/ZnO composite due to asymmetric and symmetric stretching vibration of COO–Zn (Vidhya et al. 2015). Meanwhile, another band near wavenumber 1024.21 cm^{-1} also indicated the formation of composite (Xiong et al. 2013).

3.3 Water absorption

Table 1 Effect of ZnO precursor contents on the water absorption of CA-CPL/ZnO nanocomposite

	0%	1%	1.5%	2%	2.5%
Water absorption rate (%)	dissolved within 1 h	232.0	125.0	43.9	—

"—" represent that the film containing 2.5% precursor was thin and rough and it was difficult for measure.

As shown in Table 1, CA-CPL nanocomposite film was easily dissolved in water. After introduction of ZnO nanoparticle, water absorption of composite films was decreased. Moreover, with an increasing of ZnO content range from 1% to 2%, water resistance presented a corresponding increased. It was contributed to the reducing of hydrophilic group and the increasing of hydrophobic group. In alkaline medium, the positively charged zinc complexes would be adsorbed onto the oppositely charged surface of casein micelles and COO–Zn complexes was formed by the electrostatic interaction. The reducing number of carboxyl relatively would be beneficial to reduce hydrophilic group. Moreover, silane coupling agent used to increase the compatibility between organic and inorganic phase was beneficial to increase the number of hydrophobic group. Thus casein-based ZnO nanocomposite with superior water resistance was obtained.

3.4 Antibacterial activity

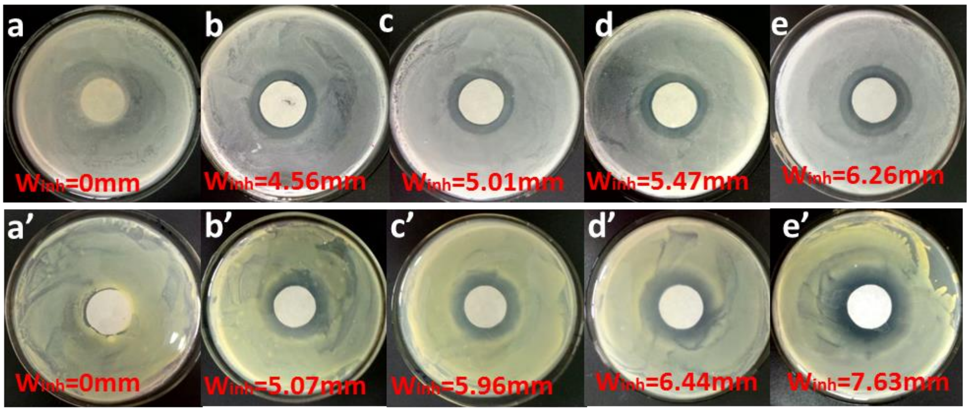
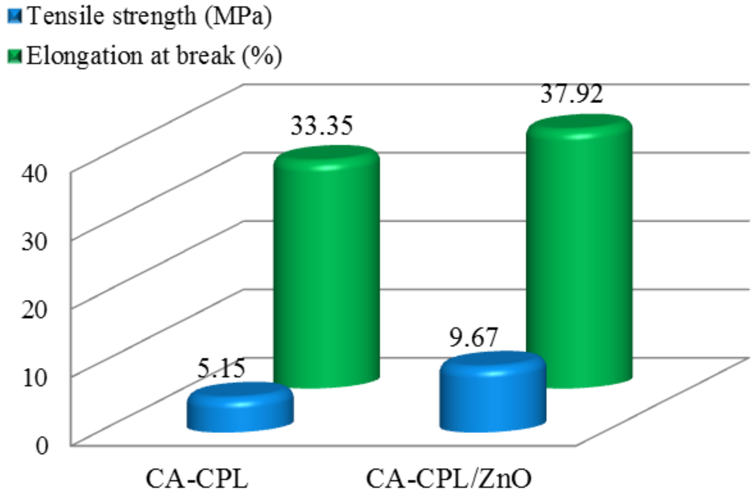


Fig.4 Effect of ZnO precursor contents on the antibacterial property of CA-CPL/ZnO nanocomposite, (a-e) E.coli and (a' - e') S. aureus: (a, a') 0%; (b, b') 1%; (c, c') 1.5%; (d, d') 2%, (e, e') 2.5%

Fig. 4 shows the inhibition activity of CA-CPL/ZnO nanocomposite against E. coli and S. aureus. The diameter of inhibition zone shown could directly demonstate the effect of antibacterial property. After incubating 2 days, CA-CPL composite was entirely spoiled by E. coli and S. aureus. However, the participation of ZnO NPs endowed the CA-CPL composite with antibacterial activity and an obvious inhibition zone was formed. With increase of ZnO content, inhibition zone was more obvious than that of low content. Moreover, the Gram-negative bacteria E. coli was less affected by ZnO than the Gram positive bacteria S. aureus. The nature of the cell wall structure was one of possible reasons for the sensitivity. S. aureus is composed of multilayers of peptidoglycan with an abundant amount of pores that renders them more susceptible to reactive species, leading to the cell disruption. The cell wall of E. coli is relatively thin and is mainly comprised of peptidoglycan, while the outer layer consists of lipopolysaccharide, lipoprotein, and phospholipids, which would be less vulnerable to the attack of reactive species (Fu et al. 2015).

3.5 Leather Finishing Application



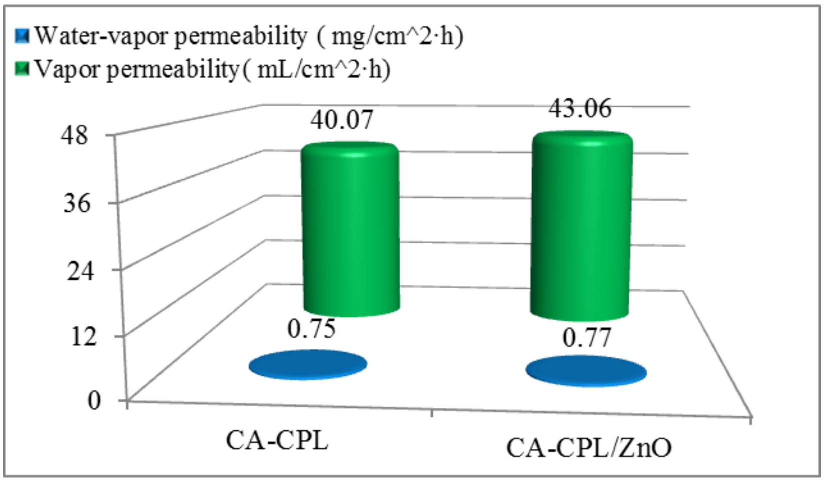


Fig.5 Mechanical property and sanitation property of leather finished by CA-CPL and CA-CPL/ZnO

Figure 5 presents the mechanical property and sanitation properties of leather finished by CA-CPL and CA-CPL/ZnO nanocomposites. As shown in Fig.5, ZnO nanoparticles had a distinct effect on the mechanical property of leather samples since tensile strength and elongation at break was increased by 87.77% and 13.7% respectively. It was mainly attributed that ZnO NPs have a relatively high elastic modulus and available surface area thus it frequently acts as a mechanical reinforcement in combination with various polymers. After introduction of ZnO, it was beneficial to obtain an efficient inter-facial interaction between ZnO NPs and casein matrix which may prompt a good stress transfer. A slight increase on vapor permeability and water-vapor permeability of leather samples was mainly due to the irregular surfaces as well as the formation of channels in the film, which was favorable for the penetration of vapor and water-vapor through the film (Liu et al. 2014).

4. CONCULSION

Casein-based ZnO nanocomposite was prepared via in-situ conversion of precursor zinc acetate. The particle size of hybrid latex was enlarged with the increase of precursor content. The results showed that casein-based ZnO nanocomposites harbor superior water resistance and excellent antimicrobial activity against E. coli and S. aureus. Leather finishing application indicated that leather samples finished by CA-CPL/ZnO nanocomposites possessed superior mechanical property and sanitation properties.

5. ACKNOWLEDGEMENTS

This work was supported by Key Scientific Research Group of Shaanxi Province (2013KCT-08), National Science Foundation of China (21504049).

6. REFERENCES

[1] A. El. Shafei, A. Abou-Okeil, ZnO/carboxymethyl chitosan bionano-composite to impart antibacterial and UV protection for cotton fabric, Carbohydrate Polymers, 2011, 83, 920–925.

[2] Jianzhong Ma, Qunna Xu, Jianhua Zhou, Jing Zhang, Limin Zhang, Huiru Tang, Lihong Chen, Synthesis and biological response of casein-based silica nano-composite film for drug delivery system, Colloids Surf. B, 2013, 111, 257–263.

[3] Qunna Xu, Fan Zhang, Jianzhong Ma, Congsheng Guo, Tao Chen, Synthesis of casein-based TiO_2

hybrid emulsion and its self-cleaning property, J. Funct. Mater. 2015, 21, 20169–20175.

[4] Mujeeb Rahman P;K. Muraleedaran;V.M. Abdul Mujeeb, Applications of chitosan powder with in situ synthesized nano ZnO particles as an antimicrobial agent, International Journal of Biological Macromolecules, 2015, 77, 266-272.

[5] Shaolan, Ding, Xiaoming, Luo, Analysis and Test of Leather Products, China Light Industry, Beijing, 2010.

[6] S.W. Cho, M. Skrifvars, K. Hemanathan, P. Mahimaisenan, K. Adekunle, Regenerated cellulose fibre reinforced casein films: effect of plasticizer and fibres on the film properties, Macromol. Res. 2014, 22, 701–709.

[7] K. Vidhya, M. Saravanan, G. Bhoopathi, V. P. Devarajan, S. Subanya, Structural and optical characterization of pure and starch-capped ZnO quantum dots and their photocatalytic activity, Appl. Nanosci. 2015, 5, 235–243.

[8] Xiaopeng Xiong, Jiangjiang Duan, Yong Wang, Zhaoju Yu, Novel hierarchical microparticles super-assembled from nanoparticles with the induction of casein micelles, J. Nanopart. Res. 2013, 15, 1-11.

[9] Feiya Fu, Lingyan Li, Lianjie Liu, Jun Cai, Yaping Zhang, Jinping Zhou, and Lina Zhang, Construction of cellulose based ZnO nanocomposite films with antibacterial properties through one-step coagulation, ACS Appl. Mater. Interfaces, 2015, 7, 2597–2606.

[10] Junli Liu, Jianzhong Ma, Yan Bao, John Wang, Huiru Tang, Limin Zhang. Polyacrylate/Surface-Modified ZnO Nanocomposite as Film-Forming Agent for Leather Finishing. International Journal of Polymeric Materials and Polymeric Biomaterials, 2014, 63, 809–814.

ACSIL O-08

IONIC LIQUIDS: NEW AGE "DESIGNER" CHEMICALS FOR LEATHER PROCESSING

N Nishad Fathima*, Aafiya Tarannum, A Jaya Prakash, GC Jayakumar, J Raghava Rao,

Inorganic and Physical Chemistry Laboratory, Central Leather Research Institute, Council of Scientific and Industrial Research, Adyar, Chennai 600020, India

** Email: nishad.naveed@gmail.com; nishad@clri.res.in*

Ionic liquids (ILs), the greener solvent media are regarded as preferential candidates for instigating desired effect on proteins due to the easy tunability of cation and anion. The use of these "designer" and "greener" solvents in leather processing has been explored in this study. Herein, we report the investigations carried out on collagen at different hierarchical level using various ILs. The conformational stability of collagen at the molecular level, thermal and dimensional stability at the inter-fibrillar level and fibre structure at skin matrix level using different types of ILs viz., imidazolium, choline, ammonium and phosphonium as cations with different anions have been studied in detail. Almost all ILs with the exception of choline destabilised collagen at fibrillar and skin matrix level. Imidazolium IL made no changes at molecular level whereas ammonium and phosphonium based ILs even altered the secondary structure of collagen. Imidazolium based ILs were explored as unhairing cum fibre opening agents thereby eliminating the use of lime and sodium sulphide during leather processing. Choline based ILs stabilised collagen and hence tanning using choline salts has been attempted. Thus, ionic liquids have been evidenced to have both stabilising and destabilising effects on collagen and the properties can be garnered and fine tuned for various applications in leather processing. Future leather production will evince interest in the use of ionic liquids as advanced chemicals for making the leather processing cleaner and greener.

Keywords: Collagen; Ionic liquids; Thermal stability; Conformational stability; Unhairing; Fiber opening; Tanning

1. INTRODUCTION

Ionic liquids are molten salts comprised of cations and anions, and are liquid at room temperature [Fujita et al. 2005]. Their high tunability, miscibility with water and solvents, low or negligible vapor pressure, high ionic conductivity, non-inflammability and striking catalytic properties makes them attractive for wide array of applications ranging in as media for green synthesis [Moniruzzamana et al. 2010] to the electrolytes phases for biosensors [Wei et al. 2008], from the precipitating agents or additives for proteins crystallization [Shamsi et al. 2007] to the mobile or stationary phase separation in separation studies [Judge et al. 2009]. Different classes of ionic liquids include the organic cations imidazolium, ammonium, phosphonium, sulfonium, pyrrolidinium, pyridinium with weakly coordinating anions viz., chloride, bromide, iodide, acetate, hexafluorophosphate and tetrafluoroborate.

Collagen, a significant structural protein has extensive applications in the field of tissue engineering such as matrices and scaffolds. It has been used as protein dietary supplements, food additives, edible film and coatings apart from it being the primary leather making protein. This emphasizes the need to understand the interaction of collagen with various additives, as they will have significant implications in food, pharma and leather industry [Hashim et al. 2015, Lee et al. 2001 and Jaya Kumar et al. 2015]. Although, interaction of ionic liquids with protein is not widely understood and there are speculations that ILs follows Hofmeister's series [Collins 2004].The kosmotropic and chaotropic ions alter the hydration network of protein, thus having a stabilizing or destabilizing effect on the protein [Zhang et al. 2006].

The interaction of collagen has been studied with various ionic liquids such as imidazolium, phosphonium and choline dihydrogen phosphate. Imidazolium IL was demonstrated to influence collagen at different hierarchical ordering [Mehta et al. 2014]. Ammonium [Tarannum et al. 2016] and phosphonium ionic liquid with variable anions also substantiates destabilizing effect on collagen due to the chaotropicity of anions [Tarannum et al. 2016], whereas choline dihydrogen phosphate, a biocompatible ionic liquid was observed to stabilize collagen by exerting an electrostatic force on collagen, thus making it a potential biocompatible crosslinker [Mehta et al. 2015].

Therefore the objective of this work is to investigate the effect of ILs on type I collagen at different hierarchical ordering *viz.,* the molecular, inter-fibrillar and skin matrix level. The secondary structural changes were monitored using circular dichroic spectroscopy, fourier transform infrared spectroscopy and thermal stability was determined using differential scanning calorimetry. The effect of ILs on higher order structure of collagen viz. skin matrix was also studied. Choline dihydrogen phosphate (CDHP), a biocompatible ionic liquid, was explored as a possible tanning agent. Molecular interaction of IL with collagen fibres was found to stabilize the protein against heat and enzymes. The effect of choline dihydrogen phosphate has been proved to be an effective crosslinking agent; therefore combination tanning has been carried out to opt for less chrome tanning system (LCTS). Also, ionic liquids were used as an auxiliary chemical for leather dyeing in order to improve the sustainability of the dyeing process. 1-butyl-3-methyl imidazolium chloride (BMIM Cl) was used as an additive along with dye. Final processed leathers were evaluated for physical and organoleptic properties.

2. MATERIALS AND METHODS

2.1 Materials

Ionic liquids, 1-butyl-3-methylimidazolium chloride (BMIM Cl), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM BF_4), choline dihydrogen phosphate (CDHP), diethyl methyl ammonium methane sulfonate (AMS), tributyl methyl phosphonium methyl sulfate (PMS), tributyl ethyl phosphonium diethyl phosphate (PEP) and choline sulfate were purchased from Ionic Liquid Technologies GmBH (IoLiTec). All leather chemicals are of commercial grade.

2.2 Isolation of type I soluble collagen

Tails of six month old albino rats (Wistar strain) were excised for the extraction of high purity type I collagen. The teased collagen fibers were washed thoroughly with 0.9% NaCl at 4°C, followed by purification with 5% Sodium chloride. The obtained precipitate was collected by centrifugation. The dialysis was then carried out extensively against 50mM phosphate buffer. After dialysis, the collagen was re-dissolved in 0.5 M acetic acid followed by final dialysis against 0.05 M acetic acid. The concentration of collagen in solution was determined through hydroxyproline content by Woessner method [Woessner 1961]. Purity of collagen solution was confirmed using SDS-PAGE electrophoresis. The stock collagen solution was diluted using 50 mM acetate buffer (pH 4.0) for further experiments.

2.3 Treatment of collagen with ILs

2.3.1 Molecular level: The concentration of collagen solution used in this study was 0.8 mg/ml. The experiments were performed by treating collagen solution with varied concentration of ILs.

2.3.2 Inter-fibrillary level: Rat tail tendons was teased from tails of six month old albino rats (Wistar strain) and were washed with 0.9% Nacl and millipore water at 4˚C. The RTT fiber were further treated with ILs and incubated at room temperature for 24 hours.

2.3.3 Skin matrix level: For treatment of ILs on skin matrix, the butt area of goat skin was taken and assessed for various parameters.

3. DIFFERENT HIERARCHICAL ORDERING OF COLLAGEN

3.1 Molecular level

3.1.1 CD spectroscopic studies

The circular dichroic spectra of collagen can be detected under nitrogen atmosphere in the far UV region ranging from 190 to 260 nm using Jasco 815 Circular Dichroism Spectropolarimeter. Approximately, 400 µl of native collagen and collagen treated ILs was scanned with 0.2 nm intervals with a path length 1 mm at 25°C with computer averaged three scans for each sample. The data were obtained in milli degrees and further converted to molar ellipticity (deg.cm^2. dmol^{-1}). Molar ellipticity was plotted against wavelength in nanometers (nm).

3.1.2 FT-IR studies

The native collagen and ILs treated collagen samples were lyophilized under pressure of 6.4 Pa at -40˚C. Lyophilized samples were taken to study the interactions between collagen and ILs using Jasco FT/IR-4200 (Fourier Transform Infrared Spectrometer) by KBr pellet method at 25°C with 60 scans in the range of 4000-400 cm^{-1} with resolution of 4 cm^{-1}.

3.2 Fibrillar level

3.2.1 Dimensional and thermal stability of RTT collagen fibers

Rat tail tendons were treated with ILs for 24h at 25°C and the changes in the dimensional stability were monitored under Aven Inc., Digital Mighty Scope, 1.3 M (Product code: 48708-25, Made in Taiwan) of 10x resolution.

The thermal stability of native and ionic liquid treated fibers was also confirmed using hydrothermal micro-shrinkage tester. A small strip of native and ionic liquids treated RTT fibers were cut and placed on a grooved microscopic slide along with appropriate medium. The slide was then placed on heating stage, which was kept under the microscope. The temperature at which fiber shrinks to one-third of its length was taken as the shrinkage temperature, T_s.

3.3 Skin matrix level

3.3.1 Treatment of ILs at skin matrix

Choline dihydrogen phosphate has been proved to be an effective crosslinking agent; therefore combination tanning has been carried out to opt for less chrome tanning system (LCTS). Different percentages of IL has been offered (0-1%) during chrome tanning process with 4% BCS. Shrinkage temperature of experimental leathers were found to be in the range of 100-110˚C similar to that of control leathers (without IL). Detailed description of leather processing is mentioned in table 1.

Leather dyeing is a challenging unit process due to their selection and addition of chemicals in post tanning. The uniform distribution of the dye and shades of leather is a foremost task; to achieve this dyeing auxiliary chemicals are usually added. In order to improve the sustainability of the dyeing process, the dyeing of leather was carried out using 1-Butyl-3-methyl immidazolium chloride (BMIM Cl), an auxiliary chemical. It was added as a pretreatment and additive along with dye. The leathers treated with BMIM Cl showed uniform shades when compared to the control leathers. Further, studies on interaction between dye and ionic liquid would provide more feasibility in leather dyeing. Detailed description of leather processing using BMIM Cl is mentioned in table 2. Goat wet blue leathers were neutralized to pH 5.5 and post tanning operation was carried out. Metal complex dye was offered along with different concentrations of BMIM Cl to check the uniform distribution of dye on the surface of the leather. Finally, after fixing with formic acid leathers were rinsed and piled.

Table 1: Chrome tanning process

Process	**Chemical**	**Percentage (%)**		**Time (min)**	**Remarks**
Tannin		Control	Experiment		
	Pickle Water	40	40		
	BCS	4	4	40	
	CDHP	-	X	30	
	Sodium Formate	0.5	0.5	30	
	Sodium Bicarbonate	1.3	1.3	3 feeds 10+30	pH set to 4, Drain/Wash/Drain

X=0.25, 0.5,0.75,1

Table 2: Post tanning process

Process	**Chemical**	**Percentage (%)**		**Time (min)**	**Remarks**
Neutralization		Control	Experiment		
	Water	100	100		
	Sodium Formate	0.5	0.5	30	
	Sodium Bicarbonate	0.3	0.3	10+30	pH set to 5.5, Drain/Wash/Drain
Post tanning					

Water	100	100		
Dye	1	1	30	Check exhaustion
BMIM Cl	-	X	30	
Synthetic fatliquor	8	8	40	
Formic Acid	3	3	3 feeds*10 +30	Drain, rinse and pile

X=0.5 and 1

4. Results and Discussion

4.1 Circular dichroism studies accrediting changes on secondary structure of collagen

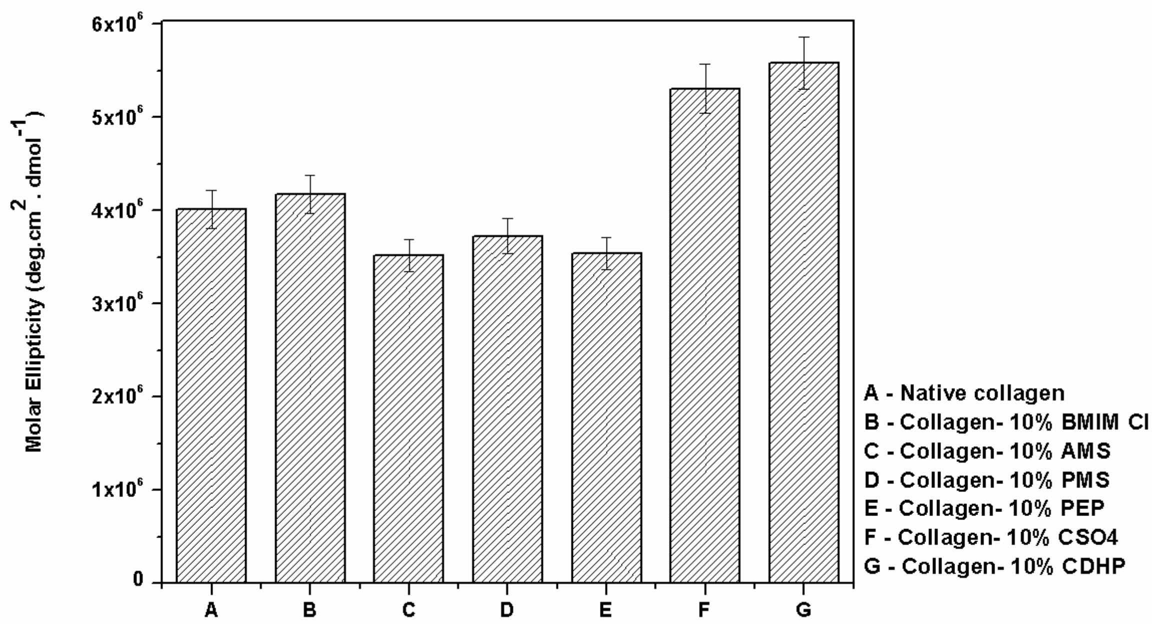


Figure 1. Effect of ILs on the secondary structure of collagen using circular dichroism

Circular dichroism is an excellent method for rapidly evaluating the secondary structure, folding and binding properties of proteins. In the far UV region, pure collagen exhibit its minimum at 197 nm and maximum at 222 nm, indicating a typical Polyproline type II (PP II) conformation [Wang et al. 2004]. In figure 1, a plot of molar ellipticity values of collagen treated with different ionic liquids at 222 nm is shown. It was observed that the molar ellipticity of collagen treated with BMIM Cl show tenuous effect, when compared to native collagen. There was a sharp decrease in molar ellipticity values for AMS, PMS and PEP treated collagen indicating the interaction of ILs with functional groups of collagen indicative of structural deformation. Albeit, there was a remarkable increase in the molar ellipticity values of collagen treated with choline dihydrogen phosphate (CDHP) and choline sulfate (CSO4), suggesting stabilization of secondary structure of collagen. This kind of behavior of stabilization or destabilization of collagen can be due to the kosmostropicity or chaotropicity of anions, which are responsible in altering the hydration shell around the collagen.

4.2 FT-IR studies accrediting changes on alteration of functional groups of collagen

Collagen shows characteristic FT-IR spectrum, with absorption bands of C=O stretching at 1640 cm^{-1} for Amide I, N-H bending and C-H stretching at 1560 cm^{-1} for amide II, carboxyl OH at 1240 cm^{-1} for amide III [Chen et al. 2010; Belbachir et al. 2009], which are characteristic of the secondary structure of collagen triple helix (Table 3). It is known that amide I and II bands are attributed to polyproline type II structure of collagen. The presence or absence of peaks within the region unveils the structural information regarding the molecule. Treatment of collagen with imidazolium ILs show tenuous effect on the amide I, II and III bands. A shift in amide I band was observed from 1642 cm^{-1} in native to 1659 cm^{-1} in the presence of choline dihydrogen phosphate. Also, there were shift in peaks for choline sulfate from 1652 cm^{-1} for amide I, 1566 cm^{-1} for amide II and 1261 for amide III. It suggests the crosslinking effect stabilizing the helices of collagen. Also, a change in Amide A band was observed. Shift in amide A band indicates that there is an increased H-bonding occurring in collagen in the presence of choline dihydrogen phosphate and choline sulfate suggesting increased physical crosslinks between collagen and choline based anions. Treatment of collagen with AMS, PMS and PEP show little shifts in amide I, II bands suggesting the changes in the microenvironment of collagen upon its interaction, albeit there was an abrupt change witnessed for amide III bands (from 1240 cm^{-1} to 1235 cm^{-1}) indicating a plausible interaction of collagen with ionic liquids, altering the micro-environment of collagen. Changes in the position of amide bands of collagen indicate the altered secondary structure oninteraction of IL with collagen accentuating structural deformation.

Table 3. Effect of ILs on the band positions of collagen using FTIR spectroscopy

Bands	Native	BMIM Cl	AMS	PMS	PEP	CSO4	CDHP
A	3370	3323	3284	3284	3284	3421	3414
B	-	-	-	-	-	-	-
I	1642	1637	1642	1643	1642	1652	1659
II	1560	1563	1561	1563	1558	1566	1561
III	1240	1240	1235	1239	1237	1261	1241

4.3 Dimensional and thermal studies accrediting changes on RTT collagen fibers

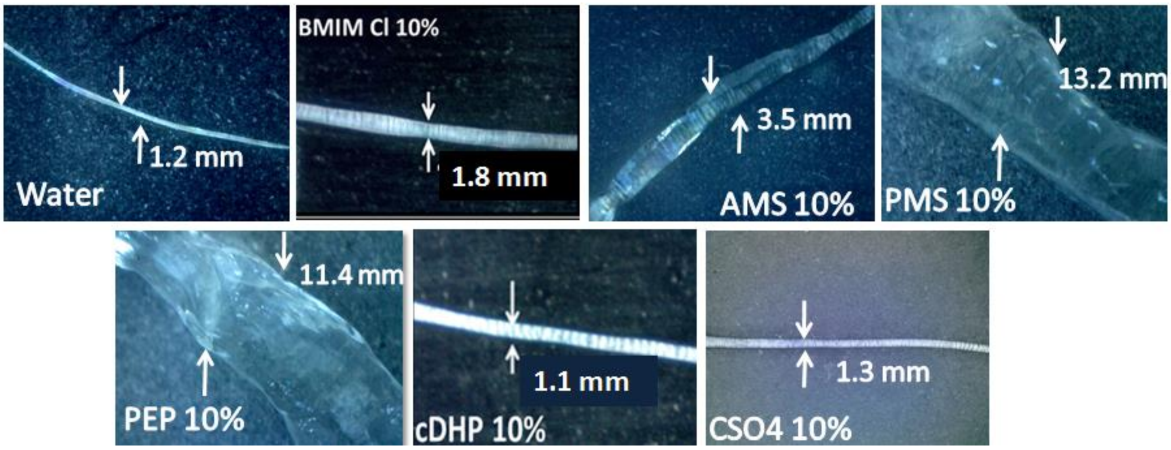


Figure 2. Effect of ILs at the inter fibrillar level: RTT treated with ILs after 24 hours at 25°C

Table 4. Shrinkage (T_s) temperature for RTT collagen fibers

Codes	T_S (°C)
Water	54±2
10% BMIM Cl	43±2
10% AMS	40±2
10% CSO4	58±2
10% CDHP	58±2

Rat tail tendons (RTT) known to be the rich source of type I collagen fibers, were excised from albino rats. It shows the characteristic macroscopic banding pattern in aqueous medium that reveals the helicity of fibrils [Chandrakasan et al. 1976]. The integrity of RTT can be viewed as continuous wave like banding pattern, indicating helical microstructure. Figure 2 connotes treatment of RTT with ILs unveiling the impact on dimensional stability of RTT collagen fibers. Compared to control, a slight swelling was observed in RTT treated with imidazolium ILs. This swelling could be due to increased surface tension at the water-IL interface. No swelling effect of choline dihydrogen phosphate and choline sulphate was observed on RTT, indicating negligible changes in RTT collagen fibers. AMS, PMS and PEP explicates the huge impact on dimensional stability of RTT collagen fibers. A distortion in wave pattern was observed within the hour of incubation. This could be due to the chaotropicity of anions and high ionic strength that alter the structure of water molecule, which leads to distorted wave pattern. Thus, it results in agglomeration and destabilization of RTT collagen fibers.

Table 4 unveils the thermal stability of RTT collagen fibre, when treated with different ILs and it was carried out using hydrothermal microshrinkage tester. The shrinkage temperature of RTT treated with 10% BMIM Cl was found to be 54°C. An increase in concentration of imidazolium IL treatment was accompanied by decreased thermal stability of RTT. Even at lower concentrations, imidazolium ILs offer only marginal stability compared to native RTT in aqueous medium. Also, there was an increase in thermal stability for choline based anions around 58°C. This increase in thermal stability suggests that choline based anions is likely to be involved in strengthening the integrity by promoting increased physical crosslinks between collagen and its hydration shell.

4.4 Tanning using ionic liquid

Conventional chrome tanning was carried out with less chrome tanning agent and with the pretreatment using IL as a tanning aid chemical. Different percentages of IL were offered with an increment of 0.25 to 1%. After tanning, leathers were analyzed for shrinkage temperature. Control and experimental leathers resisted temperatures in the range of 100-110°C. Visual assessment of final wet blue leathers were analyzed and found to be satisfactory and ratings are given in the Table 5. From figure 3, it was observed that the experimental leathers were lighter in colour than the conventionally processed leathers. With less chrome tanning agent, a significant increase in hydrothermal stability was attained using IL as a tanning aid.

Table 5. Organoleptic properties of dyed leathers

	1C	1E	2C	2E	3C	3E	4C	4E
Colour	7	8	7	8	7	8	7	8
Grain Smoothness	8	9	8	9	8	9	8	9
Softness	7	8	7	8	7	8	7	8

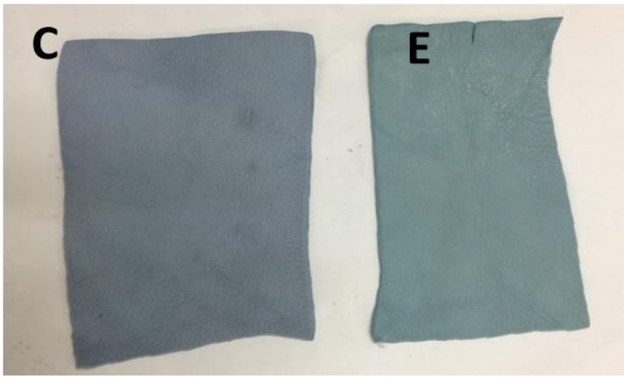


Figure 3. Effect of CDHP on wet blue leathers (4% BCS & 1%)

4.5 Leather dyeing assisted with ionic liquid

Colour values are measured by just noticeable difference (JND) value and ΔE values above the 3.9 are considered as perceivable change in colour, which can be clearly recognized by the human eye. Experimental leathers showed ΔE values higher than the counter parts as given in table 6. Post tanned leathers were assessed for their colour values and organoleptic properties. From table 7, it was observed that dye uniformity, dye intensity, grain smoothness and softness properties were in par with conventionally processed leathers.

Table 6. Colour measurement values of dyed leathers

	1 C	1 E	0.5 C	0.5 E
*L	42.207	59.547	39.910	52.496
*a	24.983	19.254	24.664	22.505
*b	26.517	17.784	25.051	24.147
ΔE	-	20.243	-	12.586

Table 7. Organoleptic properties of dyed leathers

	1 C	1 E	0.5 C	0.5 E
Uniformity	7	8	7	8
Dye intensity	8	7	8	7
Grain Smoothness	8	9	8	9
Softness	7	8	7	8

5. CONCLUSION

Ionic liquids are said to be preferential candidates for their easy tunability of cations and anions making it unique for broader applications. As they are task-specific and green solvents, it is an emerging area of interest for biotechnological and biomedical applications. It can be seen from this study that imidazolium, phosphonium and ammonium ILs combined with chaotropic anions show a destabilizing effect on collagen. However, choline ion combined with a kosmotropic anion demonstrated a stabilizing effect on collagen. It is important to note that anion plays a greater role in altering the hydration shell of collagen. It clearly suggests that the anion interaction with protein leads to the burial of hydrophilic environment followed by aggravation and protein unfolding.

Ionic liquids have been considered as new age materials for leather processing. Combination tanning was effectively carried out using CDHP and BMIM Cl was utilized for dyeing operations. However, an elaborate study on pre-tanning and post tanning operations with ILs would aid in understanding and improving the underlying mechanism and will further open avenues for the leather fraternity, marking the beginning of new era in green technology to meet the existing environmental concerns faced by the leather industry today.

6. ACKNOWLEDGEMENTS

We thank CSIR – Research Initiatives for Waterless Tanning (RIWT) project for providing the fellowship.

7. REFERENCES

1. Belbachir K, Noreen R, Gouspillou G, Petibois C, Collagen Types Analysis and Differentiation by FTIR Spectroscopy, *Anal. Bioanal. Chem*. 2009, **395**, 829-837.
2. Chandrakasan G, Torchia D A, Piez K A, Preparation of Intact Monomeric Collagen from Rat Tail Tendon and Skin and the Structure of the Nonhelical Ends in Solution, *J. Biol. Chem.* 1976, **251**, 6062-6067.
3. Chen X, Liu J, Wang J, Ionic Liquids in the Assay of Proteins, *Analytical Methods*, 2010, **2**,1222-1226.
4. Collins K D, Ions from the Hofmeister Series and Osmolytes: Effects on Proteins in Solution and in the Crystallization Process, *Methods*, 2004, **34**, 300-311.
5. Fujita K, MacFarlane D R, Forsyth M,*Chem. Commun*. 2005,**38**, 4804-4806.
6. Hashim P, Ridzwan M, Bakar M S, Hashim D, Collagen in Food and Beverage Industries. *Int. Food Res. J.* 2015, **22**, 1-8.
7. Judge R A, Takahashi S, Longnecker K L, Fry E H, Zapatero C A, Chiu M L, Ionic Liquids in Biotransformations and Organocatalysis. *Cryst. Growth. Des.* 2009, **9**, 3463–3469.
8. Jayakumar G C, Mehta A, Rao J R, Fathima N N, Ionic Liquids: New Age Materials for Eco-friendly Leather Processing. *RSC Adv*. 2015, **5**, 31998-32005.
9. Lee C H, Singla A, Lee, Yugyung, Biomedical Applications of Collagen. *Int. J. Pharm.* 2001, **221**, 1-22.
10. Mehta A, Rao J R, Fathima N N, Effect of Ionic Liquids on the Different Hierarchical Order of Collagen. *Colloids Surf., B.* 2014**, 117**, 376-382.
11. Mehta A, Rao J R, Fathima N N, Electrostatic Forces Mediated by Choline Dihydrogen Phosphate Stabilize Collagen. *J. Phys. Chem. B* 2015, **119**, 12816-12827.
12. Moniruzzamana M, Nakashimab K, Kamiyaa N, Goto M, Recent Advances of Enzymatic Reactions in Ionic Liquids. *Biochem. Eng. J.*2010, **48**, 295-314.

13. Shamsi S A, Danielson N D, Utility of Ionic Liquids in Analytical Separations.*J. Sep. Sci*.2007, **30**, 1729–1750.
14. Tarannum A, Muvva C, Mehta A, Rao J R, Fathima N N, Phosphonium based Ionic Liquids-Stabilizing or Destabilizing Agent for Collagen? *RSC Adv*. 2016, **6**, 4022-4033.
15. Tarannum A, Muvva C, Mehta A, Rao J R, Fathima N N, Role of Preferential Role of Ammonium Ionic Liquid in Destabilization of Collagen. *J. Phys. Chem. B* 2016, **120**, 6515-6524.
16. Wang Y, Li H,Han S, A Theoretical Investigation of the Interactions between Water Molecules and Ionic Liquids, *J. Phys. Chem. B*, 2004, **110**, 24646-24651.
17. Wei D, Ivaska A, Application of Ionic Liquid in Ionic Liquid Sensors. *Anal. Chim. Acta.* 2008, **607**, 126–135.
18. Woessner J F,The Determination of Hydroxyproline in Tissue and Protein Samples Containing Small Proportions of this Imino Acid, *Arch. Biochem. Biophys*. 1961, **93**, 440-447.
19. Zhang Y, Cremer P S, Interactions Between Macromolecules and Ions: The Hofmeister Series, *Curr. Opi. Chem. Bio*. 2006, *10*, 658-663.

A NEW AGE CHROMIUM-MELAMINE SYNTAN: TOWARDS QUALITY UPGRADATION OF LOWER-END RAW MATERIALS

M Sathish*, P Balasubramanian, R. Aravindhan, K J Sreeram, J Raghava Rao & P Gopalakrishnan

Chemical Laboratory, Leather Processing Division, Centre for Analysis, Testing, Evaluation & Reporting Services CSIR - CLRI, and Sellam Chemicals Pvt Ltd, Email: jrrao@clri.res.in

One of the unavoidable steps in the transformation of wet-blue to finished leathers is the filling up of void spaces in the skin matrix. Drawback associated with chrome tanning, the lack of fullness is being addressed during the post-tanning process by employing synthetic tanning agents. In general, the syntans are manufactured by enhancing the molecular weight of aromatic compound such as phenol and its derivatives, melamine etc., through condensation reaction. Commercially available chromium syntan, which contains combination of chromium salt and phenol-formaldehyde condensate polymer, is employed during the rechroming process to ensure the uniform chromium content of wet-blue leather sourced from different places and also to impart fullness. However, in order to improve belly filling more amount of melamine-formaldehyde condensate is used in the subsequent re-tanning process. Liberation of free formaldehyde is one of the major limitations of the conventional synthetic tanning agent. Keeping in mind the strictures of free formaldehyde and selective filling, an attempt has been made to prepare a novel formaldehyde free chromium-melamine syntan. The prepared product has been used in the rechroming process. The product imparts selective filling/grain tightening effect on loose area/belly region and also increases the thickness without affecting the area yield. The product provides good dye levelling, excellent buffability with natural sheen, uniform milling pattern and apart from this upgradation of the lower selections with improved cutting value is also obtained.
Keywords: Chromium, Melamine, Syntan, Rechroming

1. INTRODUCTION

The hides/skins used for leather manufacturing are anisotropic in nature. Removal of non-leather making materials such as elastin, reticulin, proteoglycan, fat, etc. and carrying out various other chemical/mechanical operations on hides/skins further increases the anisotropicity. The economic value of the final leather strongly lies in the homogeneity of the substrate. Usage of vegetable tannins in leather making provides tanning cum filling action thereby increasing the homogeneity of the substrate. But today, 90% of the leather is made by using chromium (III) salt due to the limited availability of vegetable tannins[1]. Though chrome tanned leathers are superior to vegetable tanned leathers in terms of hydrothermal stability and mechanical properties, the substrate homogeneity is not obtained during chrome tanning process. In commercial language, tanners generally say “chrome tanned leathers are empty in nature”. Leather industry in countries like India[2], carry out an operation called rechroming, in order to normalize the Cr_2O_3 content in the batch of wet blues taken, which iturn results in uniform uptake of retanning chemicals by the leathers. The chromium syntan used for this operation also improves the fullness properties.

The chromium syntan used during the rechroming operations is a masked chromium(III) salt, wherein chromium-ligand complexes are coupled to condensed aromatic sulfonates. In such syntans, the preferred aromatic compound is the phenol or naphthalene and the condensation is carried out in the presence of formaldehyde as cross linker (Samir, 1987). Use of this chromium syntan results in the reduction/avoidance of aromatic syntans in subsequent post-tanning

In the case of ill fed animals, preferential belly filling is achieved in the retanning stage through use of melamine-formaldehyde condensates (Swarna et al, 2012, Sreeram et al., Patent no: 0937DEL2014) Survey of the leather chemical market indicates that melamine-formaldehyde products are devoid of metal ions. A lacuna of this kind forces the tanner to employ a variety of aromatic condensates to achieve the desired fullness, roundness etc. Keeping in view of the above overview of the leather industry and the auxiliary market, this work pertains to the application studies associated with a newly developed product – chromium based melamine condensate devoid of formaldehyde as cross-linker. Through this study, the ability of such a product to perform multiple functions, viz., normalization of chromium content in a batch of wet blue and also the improved fullness of the belly owing to the use of chrome-melamine syntan is evaluated.

2. MATERIALS AND METHODS

Chemicals used for the preparation of the chrome-melamine syntan were of commercial grade. Wet blue cow sides of Indian origin were chosen for the study and were procured from local vendor. The chemicals used for leather processing were of commercial grade and the chemicals used for analysis were of analytical grade. The quantity chemicals used was based on shaved weighed.

2.1 PREPARATION OF CHROME MELAMINE SYNTAN

2.1.1 Preparation of Melamine Resin

Melamine was mixed with 600 to 1000% v/w, of water and the resulting solution was heated to a temperature in the range of 75 to 90°C for a period in the range of 15 to 60 minutes under stirring condition to obtain melamine dispersion. Then, 35 to 110%v/v, of organic acid was added to this solution under stirring condition. This was followed by the addition of 45 to 150% v/v, of formaldehyde free crosslinking agent. Stirring was continued for a period in the range of 30 to 120 minutes to obtain transparent pale yellow color solution. Pale yellow solution was then allowed to settle for a period of 15 to 60 minutes, when the color of the solution turned dark orange.

2.1.2 Incorporation of chromium into melamine resin

Chromium(III) salt was dissolved in 500 to 1000% v/w and the solution treated with 5 to 50% w/w, of organic ligand at a temperature in the range of 70 to 90°C to obtain masked chromium salt solution. This solution was reacted with 0.1 to 1% v/v of the transparent dark orange liquid at a temperature in the range of 80 to 90°C for a period in the range of 5 to 30 minutes to obtain melamine-chrome complex liquid. This liquid was spray dried. The developed product could be represented by the general molecular formula $(C_xH_yN_6O_z)_{n}$-Cr(III),‘x’ being an integer ranging from 5 to 9, ‘y’ an integer between 8 to 12, 'z' an integer between 2 to 6 and 'n' an integer between 10-50.[6] The product is described in the subsequent text as CMS.

2.2 Characterization of CMS

The prepared chrome-melamine syntan was characterized for various properties such as pH, moisture content, total soluble matter and chrome content as per the standard procedures.7 Particle size analysis of the sample was also carried out using Malvern Zetasizer and was compared with that of the commercially available chrome syntan.

2.3 Evaluation of Chromium-Melamine Syntan in Re-chroming Process

In order to evaluate the developed chromium-melamine syntan, four wet-blue cow hides having the thickness of 1.1-1.2 mm were cut into two halves along the backbone and marked as left and right. These left and right halves were grouped separately and their weights were noted. Left halves were treated with commercial chromium syntan (Control) and right halves were taken for the experimental process where developed chromium-melamine formulation was used as re-tanning agent and the process recipe has been tabulated in Tables I.

Table 1 Evaluation of chromium-melamine syntan –Process recipe

Process	% Offer	Remarks
Acid Washing		
Water	100	
Acetic acid	1	2x10+45 min
Water	5	pH 3.0-.3.2
Re-Chroming		
Water	100	
Chromium Syntan (C or CMS)	6	60 min
Sodium formate	1	30 min
Sodium bicarbonate	1	2x10+60 min, pH 3.0-.3.2
Water	5	Pile over night
Washing		
Water	100	10 min, Drain
Neutralization		
Water	100	
Sodium formate	1	30 min
Sodium bicarbonate	1	
Water	10	3x10+30 min, pH 5.2-5.5
Re-tanning, & Fatliquoring		
Water	100	
Acrylic syntan	2	30 min
Phenolic syntan	4	
Tara powder	4	
Melamine syntan	4	90 min
Synthetic fatliquor	4	
Semi-synthetic fatliquor	4	
Water	20	2x15+60 min,
Protein Filler	2	20 min
Fixing		

Formic acid	2.5	
Water	10	3x15+30 min, Exhaustion was checked. Crust leathers were set twice, hooked to dry and staked
Note: C: Commercial chromium syntan, CMS: Chromium-Melamine syntan		

2.4 Organoleptic Properties and Physical Strength Characteristics

The control and experimental leathers were analyzed for various organoleptic properties such as fullness, softness, grain tightness, grain smoothness and roundness by experienced persons from the leather industry. They were rated on a scale of 1-10, where higher points indicate better properties. The physical properties such as tensile strength (IUP 6, 2000), percentage elongation at break, tear strength (IUP 8, 2000) and bursting strength (IUP 9, 1996) were examined for both control and experimental leathers. The specimens for various testing as mentioned above were obtained as per IULTCS standard method. Specimens were conditioned for 24 hr at 25 ± 1 °C and 65 ± 2% RH[14].

2.5 Morphological Analysis

Samples from control and experimental crust leathers were cut from the belly portion and coated with gold using an Edwards E306 sputter coater. A Quanta 200 series scanning electron microscope was used for the analysis. The grain as well as cross-section was examined under the microscope at varying magnifications. The micrographs were obtained by operating the SEM at a voltage of 30 KV with different zoom level.

2.6 Analysis of Rechrome Liquor

The spent liquor after rechroming and basification was collected from control and experimental trials and the volume was noted. The liquor was filtered and then analyzed for chromium content (%Cr_2O_3), total dissolved solids (TDS) and chemical oxygen demand (COD) as per standard procedure (Clesceri et al., 1989).

3.0 RESULTS AND DISCUSSION

3.1 Preparation of Chromium-Melamine Syntan (CMS)

CMS has been prepared by condensing melamine without using formaldehyde as crosslinking agent.[5] The prepared melamine condensate has been co-linked with masked chromium(III) sulfate. The prepared chrome melamine syntan has been used in the rechroming of wet blue cow leathers. This product has dual benefit of having chromium and melamine linked together as a single product so that retanning with chromium and filling of looser portion by melamine can be achieved at the same time. During spray drying required amount of sodium bicarbonate has been added to the liquor in order to bring the final pH of the 10% solution of CMS to be around 3.5±0.5.

3.2 Characterization of CMS

CMS has a moisture content of 10.3±0.4%, pH (10% solution) around 3.5±0.5 and Cr_2O_3 content of 12±0.5%. Particle size analysis results are depicted in Fig. 1. Intensity average diameter of CMS was observed to be around 2616 nm. The particle size of BCS and commercial chrome syntan has also been analyzed and observed to be around 1813 and 1644 nm, respectively. Thus, it could be inferred that owing to complexation with melamine, CMS has higher particle size compared to conventional BCS or commercial chromium syntan. This could probably lead to improved belly filling and firmness of the final leather.

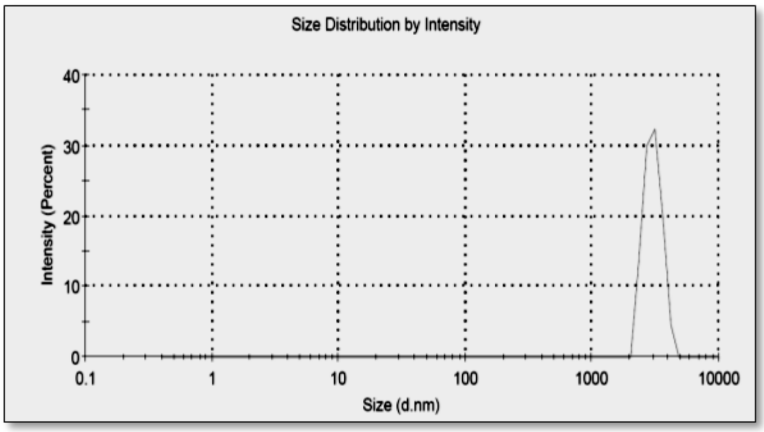


Fig.1 Particle size distribution of Chrome-melamine Syntan

3.3 Physical Testing and Hand Evaluation of Leathers

Crust leathers rechromed using CMS have been characterized for physical and organoleptic properties. Tensile, % elongation, tear strength, load at grain crack and distension at break for the control and the leathers processed CMS are given in Table II. It could be observed that the physical properties of leathers rechromed with CMS are on par with that of the control leathers and the values are higher than those of standard norms. The organoleptic properties of the crust leathers, which are rechromed with commercial chrome syntan and CMS, have been detailed in given in Table III

Fig. 2: Photographic images of control (left) and experimental crust (right) leathers

It could be clearly observed that the crust leathers rechromed using CMS showed better belly filling and improved firmness compared to the leathers rechromed with commercial chrome syntan. The images of the both control and crust leathers are depicted in Fig. 2. It could be clearly seen that both the leathers have good color uniformity. In the case of experimental leathers, there are no color patches or yellowness being found.

Table II Physical properties of control (Commercial chrome syntan) and experimental (CMS) leathers

Characteristics	Control	Experiment
Tensile Strength (N/mm^2)	23±1	21±1
Elongation at break (%)	60±1	62±1
Tear Strength	20.3±0.5	21.7±0.6
Load at grain crack (kg)	32±1	29±1
Distention at grain crack (mm)	9.10±0.2	8.70±0.2

Table III Hand Evaluation of crust Leathers rechromed using commercial chrome syntan (Control) and CMS (Experimental)

Samples	Control	Experimental
Belly filling	8±0.5	9±0.5
Fullness	7±0.5	9±0.5
Roundness	7±0.5	8±0.5
Firmness	6±0.4	8±0.5
Softness	7±1	7±1
Color uniformity	9±0.5	9±0.5
Overall appearance	7±1	9±0.5

3.4 Morphological Analysis

Grain and cross section from the belly portion of the crust leathers obtained from control and experimental process employing CMS have been analyzed using SEM (Fig. 3). Grain surface of the experimental crust leathers was found to be clean without any deposits on the surface. SEM images of the cross section of the experimental crust leather obtained from belly portions shows a compact fiber structure. This could be attributed to the filling nature of CMS. Though the control and experimental samples show comparable compactness in the fiber structure throughout the cross-section indicating uniform filling of syntan, crust leather rechromed using CMS showed more compact fiber structure.

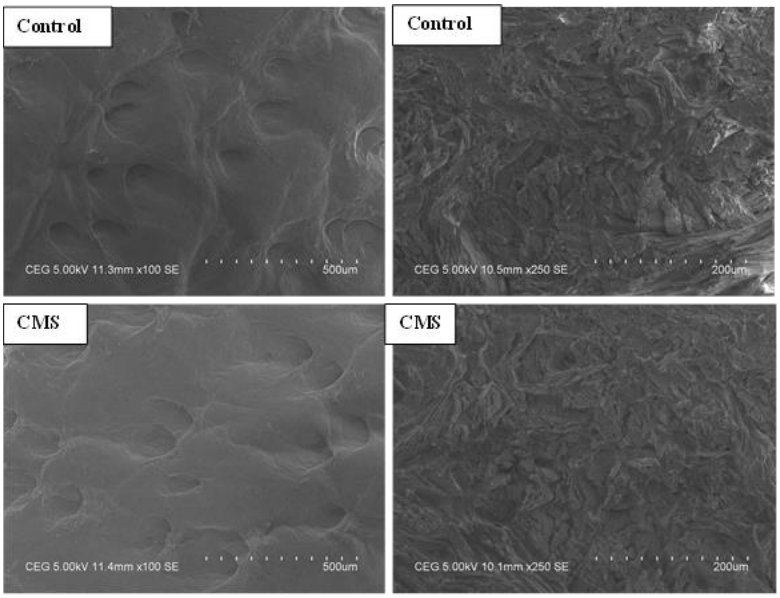


Figure 3 Scanning electron micrographs of grain and cross section of crust leathers rechromed with commercial chrome and CMS syntan

3.5 Analysis of Wastewater

TDS, COD and %Cr_2O_3 are the three parameters that have been chosen for analyzing the environmental impact of spent rechroming liquor. Results are provided in Table V. COD, TDS and %Cr_2O_3 values were on par for the wastewater from both control and experimental processes. Thus, it could be inferred that the use of CMS does not give rise to any additional pollution load.

Table V Analysis of wastewater from control and experimental process

Effluent Analysis	Chrome Syntan	CMS
TDS (ppm)	20,000±24	20,000±28
COD (ppm)	6500±12	6800±10
% Cr_2O_3	673±5	606±13

4.0 CONCLUSION:

In this work, CMS has been prepared and used in the rechroming of wet blue cow upper leather. CMS had a characteristic Cr_2O_3 content of 12±0.5%. The salient features of the leather treated with CMS are given below.

- Zero formaldehyde
- Eco-friendly with no possibility of Cr(VI)
- Selective filling and grain tightening effect on loose area and belly region
- Provides fine grain with soft handle
- Increase in thickness without affecting area yield
- Good dye leveling, excellent buffability with natural sheen
- Produces uniform milling pattern
- Overall Upgradation and better cutting value

ACKNOWLEDGEMENT

The authors acknowledge the financial support of Supra Institutional project STRAIT.

REFERENCES

1. Clesceri, L.S. Greenberg, A.E. and Trussel R. R.: Standard methods for the examination of water and wastewater, 17th ed. American Public Health Association, Washington DC (1989).
2. IUP 2 Sampling, JSLTC **84**, 303-309.
3. IUP 6, Measurement of tensile strength and percentage elongation, JSLTC **84**, 317-321, 2000.
4. IUP 8 Measurement of tear load – double edge tear JSLTC 84, 327-329, 2000.
5. Knaflic, F.; Latest aspects of retanning full grain leather, JALCA **76**, 320-329, 1981.
6. Prentiss, W.C., Sigafoos, C.R. and Tetreault, H.A.; A statistical comparison of synthetic retanning materials JALCA **73**, 31-38, 1978.
7. Samir, D.G.; Innovative tannages for improved leather JALCA **82**, 167-184, 1987.
8. SLP 9 (IUP 9), Measurement of distension and strength of grain by the ball burst test, Official Methods of Analysis, The Society of Leather Technologists and Chemists, Northampton (1996).
9. Sreeram, K.J., Sangeetha, S., Jayakumar, G.C., Rao, J.R. and Nair, B.U.; An environmentally benign organic-metal framework for single step retanning. (Indian Patent Application No. 0937DEL2014)
10. Swarna V. K., Jaya Kumar, G.C., Ram Kumar, S.C., Chandrasekaran, B., Rao, J.R. and B. U. Nair.; Studies on the development of leathers from formaldehyde- free melamine syntan JALCA, **107**, 144-150, 2012.

ACSIL O-10

NOVEL SURFACTANTS – IN LEATHER PROCESSING

V.Vijayabaskar* & J.K. Basu

Leather Chemicals, Balmer Lawrie & Co Ltd.,
Manali, Chennai

This lecture addresses mainly about surfmers – polymerisable surfactant and its copolymers used in processing of leather. There will be a discussion on novel concept of making polymerized fat using a surfmer based on renewable sources. A facile method was developed in-house containing a dispersion of a selected amphiphilic copolymer and substantially free from organic solvents. They impart light fastness characteristics, reduce fogging and minimize Cr (VI) a carcinogenic generation in leather.

Another part of this paper will cover the synthesis of novel polymer based on surfmer with carboxyl functionalities. This polymer binds the free chrome on to the collagen and Cr (VI) was below detectable limits on leather on ageing.

BACKGROUND OF THE WORK

Many chemical and mechanical operations are involved in treating hides and skins to develop leather. Two important chemical operations in the treatment of leather is fat-liquoring and retanning. Fatliquoring is used to impart the desired strength and temper properties to tanned leather. **Fatliquors** lubricate the leather fibers so that after the leather is dried its fibers are capable of sliding over one another. In addition to regulating the pliability of the leather, fatliquoring contributes greatly to the tensile and tearing strength of the leather. Retanning is done to impart good filling and other mechnical and physical properties to leather.In other words,fatliquoring and retanning in a operation is done to regulate softness and fullness of the article.

The first part of this paper deals with polymeric fatliquor which performs both as retanning and fatliquoring agents and provides the treated leather with a number of desirable properties including light fastness, strength, body etc. The main objective of the present investigation is to provide a polymer for fatliquoring as well as retanning either partially or fully which provides the treated leather with both the requisite strength and softness typically associated with the conventional fatliquors and also provide superior light fastness. There will be also significant reduction in the usage of conventional syntans and fatliquors in the processing of leathers

Another application as chrome fixing agents binding the free chrome in wet blue by incorporating the copolymers based on non-ionic surfmers have been mentioned . These copolymers prevent the oxidation of free chrome to Cr (VI) under ageing conditions

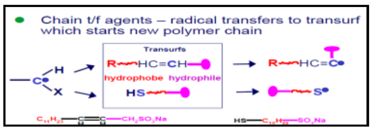
SURFMERS

The amphiphilic copolymers have been selected because of their ability to provide the leather with desirable strength and aesthetic softness characteristics and filling while reducing the total consumption of syntan and fatliquor in the recipe substantially. It was found that dispersions of these amphiphilic copolymers, preferably in the form of aqueous emulsions, are substantive, or in other words they remain in the treated leather, and provide exceptionally good light fastness even under stringent conditions. The selected amphiphilic copolymer must contain at least one hydrophobic monomer or surfmer. The term **surfmer refers to polymerisable surfactant**. Conventional surfactants are anchored on the polymer emulsion particle surface by physical forces alone and, hence their adsorption-desorption equilibrium has a crucial role in governing the stability and other characteristics of latexes prepared using them. It is desirable therefore to have the surfactants covalently bound to the polymer latex for enhanced stability and performance. This can be used by using reactive surfactants, which become an integral part of the polymer during polymerization and would selectively reside on the surface of the latex providing it the requisite stability. The area of reactive surfactants has witnessed a surge of activity during the last decade, in part because of the combined efforts of many European laboratories.

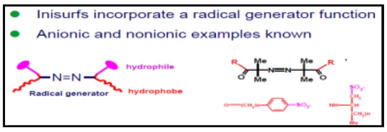
There are three types of surface active agents with polymerising capabilities used in polymer synthesis.

1. Transurf – Chain transfer agent 2. Insurf – surfactant and an initiator and 3. Surfmer – Surfactant and a monomer.
   The examples are given below

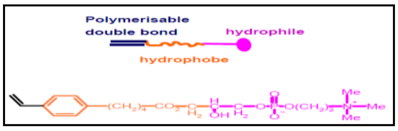
Transurf



Inisurf



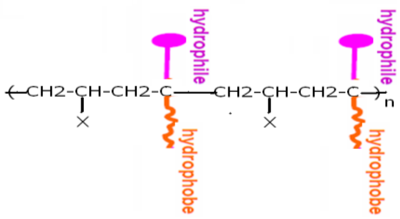
Surfmer



Some reviews provide a comprehensive summary of the current status of this field. These polymerisable surfactants have extensive applications such as in synthetic rubbers, paints, adhesives, binders, additives in paper and textiles, impact modifiers, solid phase flocculants, rheological modifiers, solid phase supports in catalysis, diagnostic assays, cell separation, and drug delivery systems. In this work an attempt has been made to utilize these class of polymers in leather treatment applications

PREPARATION OF POLYMERIC FAT PREPARATION THROUGH SURFMERS

Long chain esters with terminal vinyl groups are used as surfmers and are prepared by esterification of fatty alcohols with carboxylic acids with vinyl ends. Different esters of with carbon number varying from C-12 to C-18 were prepared. Finally it was optimized that copolymers based on lauryl esters with acrylic acid were found to give better performance as compared to other esters. Acrylic acid was used as other hydrophilic comonomer. The copolymer is prepared through inverse emulsion technique by dispersing under vigorous stirring with1 mole of hydrophilic monomer in 1.2 moles of surfmer. A very little amount of water with initiator dissolved in it is added just to form the interface.The unreacted surfmer is determined by extraction with acetone. The copolymer after acetone extraction is soluble in chloroform and can be characterized by H NMR spectroscopy. There will be more than 90% incorporation of surfmer in the copolymer composition. This process also helps in processing a copolymer with very high % solids. Such a high molecular weight polymer surfactant is very much useful in emulsifying most of the oils. The copolymer with surfmer units as its co-monomer is given below.



The final copolymer is diluted to 30% solids and used a polymeric fatliquor and retanning in leather applications. The polymerisable surfactant or surfmer is used in the present invention also act as a chrome fixing agent and thereby, reducing the percentage of chrome loading in the effluents.

PREPARATION OF LEATHERS

The evaluation of the selected polymeric **fatliquors** with lessamount of syntans and other conventional fatliquors was compared to standard recipe of known percentages of conventional syntans and fatliquors to make upper type of leather. In Trial 1 Polymeric fatliquor alone is used and compared with recipe of conventional process to make upper leathers. The physical and organoleptic properties are given Table 2 &3.

Table -1 Percentage Usage

	TRIAL 1		TRIAL 2	
	LHS	RHS	LHS	RHS
Polymeric Fatliquor	15	-	12	-
Fatliquor	-	5	-	5
Syntan	-	20	3	20

Table -2 Physical Properties

Tensile Strength(Kg/cm2)	256.25	218.9	244.78	220.89
Elongation(mm)	71	51	65	48
Grain Crack Load(Kg)	39	24	32	26
Distension 1	11.75	10.1	9.60	8.5
Bursting Load (Kg)	>65	32	>58	34
Distension 2	>12.28	11.30	>11.50	10.58
Lightfastness	Grade 4 on grey scale	Grade 3 on grey scale	Grade 4 on grey scale	Grade 3 on grey scale

Table -3 Organoleptic Properties

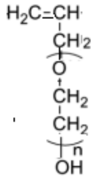
Inner softness	3.5	4.5	3.8	4.5
Fullness	4.0	4.5	4.0	4.5
Surface touch	4.5	4.5	4.5	4.5
Grain tightness	4.5	4.5	4.5	4.5
Feel	Slightly papery	Leathery	Slightly papery	Leathery

The slight papery feel could be adjusted by incorporation of little % of conventional fatliuquor in the recipe

*Evaluated on a scale of 0-5
0-poor
5-excellent
We have launched fatliquors with surfmers as co surfactants and in the process of commercializing a retan fatliquor with both filling and to provide softness to leather.

Chrome fixing agent.

A terpolymer with multiple carboxyl functionalities was prepared by solution technique radical polymerization of maleic anhydride, acrylic acid and a non-ionic surfmer with allyl ends. This polycarboxylate ether based polymer with multiple carboxyl ends binds more chromium to leather and few leather trial showed that Cr (VI) generation is avoided. The allyl polyethylene glycol ether based surfmer used is mentioned below



In this trial Table 4 , 2% ter polyme based on the pelt weight is tried as a chrome exhaustion aid

Table -4

	Trial with 2% Terpolymer	Control
Cr (VI) as per DIN ISO 17075 under ageing conditions	Nil	9 ppm
Total Chromium (Cr) content % as Chrome oxide (Cr_2O_3)	3.2	2.5

There is a 30% improvement in chromium bound to collagen with the aid of multiple carboxyl functionalities in the terpolymer. A product Balfix PAC 20 based on this approach was launched.

CONCLUSIONS

A synthetic route to prepare a polymeric fatliquor with maximum weight % of about 90 % of polymerisable surfactant- surfmer in its copolymer composition. This polymeric fatliquor functions both as a fatliquor and retanning agent matching the physical properties requirements of upper leathers. Apart from this the light fastness imparted by this fatliquor could be taken as a major advantage. This also minimises the loading of conventional fatliquors in the recipe which would result is fogging. A terpolymer based on non ionic surfmer avoids the Cr(VI) formation by binding more chromium due to probable complex formation with multiple carboxyl groups .

ACKNOWLEDGMENTS:

We sincerely thank Prof. S.Ramakrishnan , IPC , IISC , Bangalore for his technical advice in this work .

REFERENCES

1. Urqvida, M. B.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. J Polym Sci Part A: Polym Chem 1992, 30, 2619.
2. Guyot, A.; Goux, A. J Appl Polym Sci 1997, 65, 2289.
3. Lam, S.; Hellgren, A. C.; Sjoberg, M.; Holmberg, K.; Schoonbrood, H.; Unzue, M. J.; Asua, J. M.; Tauer, K.; Sherrington, D. C.; Goni, M. A. J Appl Polym Sci 1997, 66, 187.
4. Guyot, A.; Tauer, K.; Asua, J. M.; van-Es, S.; Gauthier, C.; Hellgren, A. C.; Sherrington, D. C.; Goni, M.; Sjoberg, M.; Sindt, O.; Vidal, F.; Unzue, M.; Schoonbrood, H.; Shipper, E.; Lacroix-Desmazes, P. Acta Polym 1999, 50, 57.
5. Guyot, A. Surf Sci Ser 2003, 114, 495.
6. Summers, M.; Eastoe, J. Adv Colloid Interface Sci 2003, 100, 137.
7. Pichot, C. Polym Adv Technol 1995, 6, 427.
8. Pichot, C.; Charluex, B.; Charreyre, M.; Revilla, J. Macromol Symp 1994, 88, 71.
9. Cousin, P.; Smith, P. J Appl Polym Sci 1994, 54, 1631.
10. Goodwin, J. W.; Ottewill, R. H.; Pelton, R.; Vianello,
11 G.; Yates, D. E. Br Polym J 1978, 10, 173.
12. Goodwin, J. W.; Ottewill, R. H.; Pelton, R.; Vianello, G.; Yates, D. E. Colloid Polym Sci 1979, 257, 61.
13. Goodwin, J. W.; Ottewill, R. H.; Pelton, R.; Vianello, G.; Yates, D. E. Br Polym J 1973, 5, 347.
14. van Streum, K. H.; Belt, W. J.; Piet, P.; German, A. L. Eur Polym J 1991, 27, 931.
15. Ford, W. T.; Yu, H.; Lee, J. J.; El-Hamshary, H. Langmuir 1993, 9, 1698.
16. Ionmata, Y.; Wada, T.; Handa, H.; Fujimoto, K.; Kawaguchi, H. J Biomater Sci Polym Ed 1994, 5, 293.
16. Delair, Th.; Pichot, C.; Mandrand, B. Colloid Polym Sci 1994, 272, 72.
17. Vijayabaskar, V.; Subramanian, S.R.K.; Basu, J.K.; Gunjan ; Animesh Chattopadhyay ; , Ravikumar S.; Ramakrishnan S. Filed for Indian Patent 2009.

TANNING WITH A GALLIC EXTRACT IN COMBINATION WITH A CATIONIC ESTER FOR THE PRODUCTION OF HIGH PERFORMANCE LEATHERS

Eric Poles[*], Andrea Calleri, Paolo Saccagno

Silvateam S.p.A., Leather Division Via Torre, 7 - 12080 San Michele Mondovì (CN) Italy,
Email: epoles@silvateam.com
Silvateam S.p.A., Leather Division Via Torre, 7 - 12080 San Michele Mondovì (CN) Italy,
Email: acalleri@silvateam.com
Silvateam S.p.A., Leather Division Via Torre, 7 - 12080 San Michele Mondovì (CN) Italy,
Email: psaccagno@silvateam.com

A new metal free tanning system was developed by using a modified hybrid extract from Gallnuts, Chestnut and Tara in combination with a cationic fatty ester (GEDT).
The hybrid extract obtained has self-tanning properties with a shrinkage temperature of over 80°C, a very light colour and strong light / heat fastness.
The tannage by itself with the Gallic tanning agent is very anionic but by introducing a Cationic Ester (CE) during tannage is possible to modify the reactivity of the system and the final leather has amphoteric properties. The levels of exhaustion of retanning agents, dyes and fatliquors obtained are very high as well as low COD and high biodegradability of the final effluent.
The system can be associated to traditional vegetable tanning systems and there are various ways of carrying out the tannage including recycling of the pretanning and the main tanning liquor. A mass balance of the tanning material was carried out and tannins content of the discharge liquor monitored after several batches. The final pretanning and / or tanning liquor can be recycled to the following batch to make “colouring” and exhaust the unfixed tannins prior to discharge.
By varying the retanning / fatliquoring all types of leathers can be obtained. The system works well both on bovine and small skins.
A study on the effluent of the system was carried out and the biodegradability tested in a pilot tannery’s effluent plant.

Introduction

In the leather industry, the awareness of environmental problems has increased considerably and, during recent years, protecting environment has become a global issue. In fact, regulatory pressures oblige tanners to make continuous improvements in the processing operations and consumers are looking more closely at whether hazardous substances are present in leather and leather articles. Furthermore today’s market requires a tannage that is:

- Free from Chrome salts and other metals
- Formaldehyde content less than 3 ppm
- Aldehyde free processes (in the textile industry Glutaraldehyde has already been banned)
- High heat and light resistance

- High tensile / tear strength
- In respects of MRSL (Manufacturing Restricted Substances List), ZDHCS (Road Maps to Zero Discharge)
- Low % of chlorides and sulphates processes
- Low COD processes
- Soft, tight and light weight leathers
- Good dyebility
- Process easy to scale up in production / easy manufacturing of finished products
- Low cost processes

Having thought about different solutions to match today's requirements it came to mind the marvellous most ancient system of tannage which is **"Natural Vegetable Tannage"**. The aim of this work was to develop a system of natural tannage with selected tannin agents which can match, not only the beauty of vegetable tanned leather but also the high performance values requested by the OEMs. An important part of the research has focused on the impact of the process on nature by a deep analysis of spent liquors, mass balance, recycling systems and biodegradability test to assure the sustainability of the process.

1. MATERIAL AND METHODS

- A natural tanning system was developed by using a **D**ispersed **E**llagic / **G**allic **T**annin **(GEDT)** of natural origin which has high fastness properties (Figure 1).

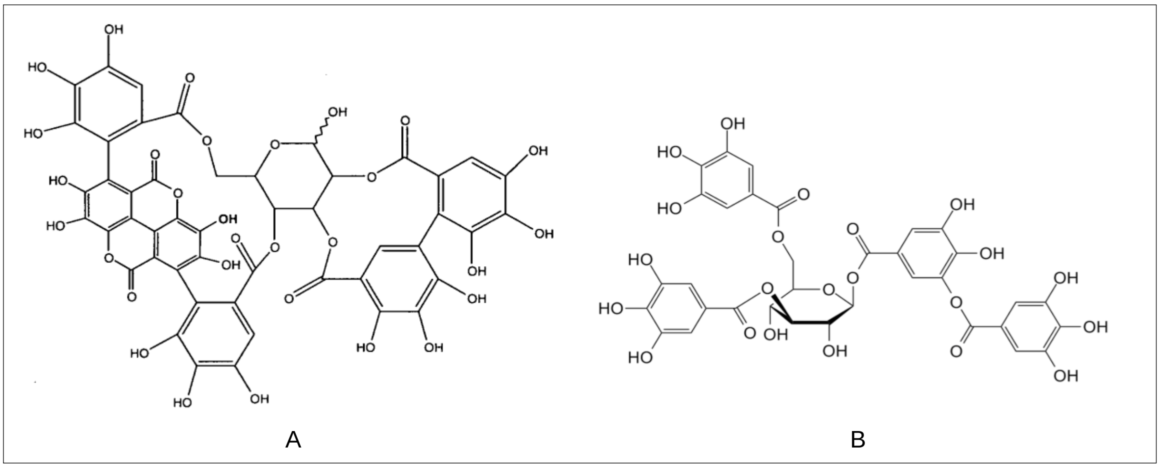


Figure 1 Chemical structure of Ellagic Tannin (A) and Gallic Tannin (B).

- **GEDT** is obtained by extraction of some natural sources, such as fruits, pods and wood rich in Gallic and Ellagic tannins. The leach extract is dispersed and hydrolysed to reduce its astringency and improve penetration (Figure 2).

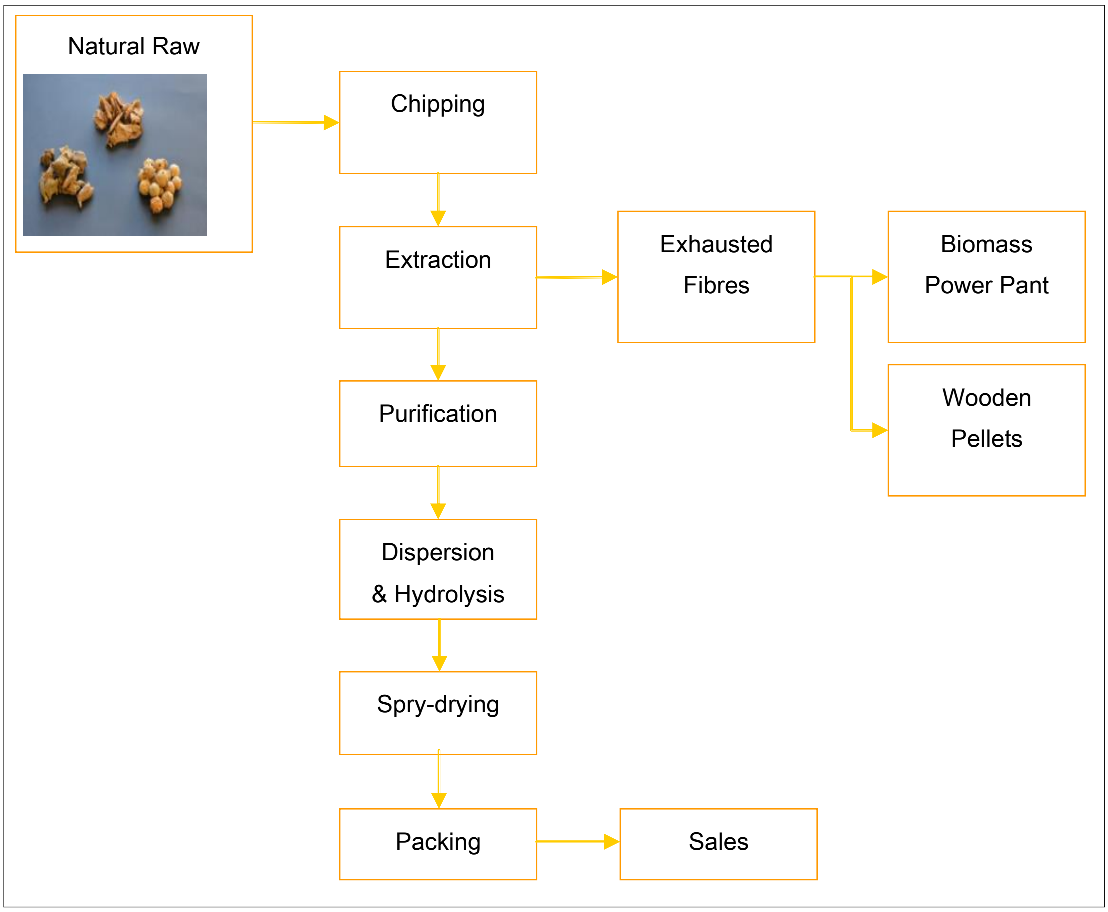
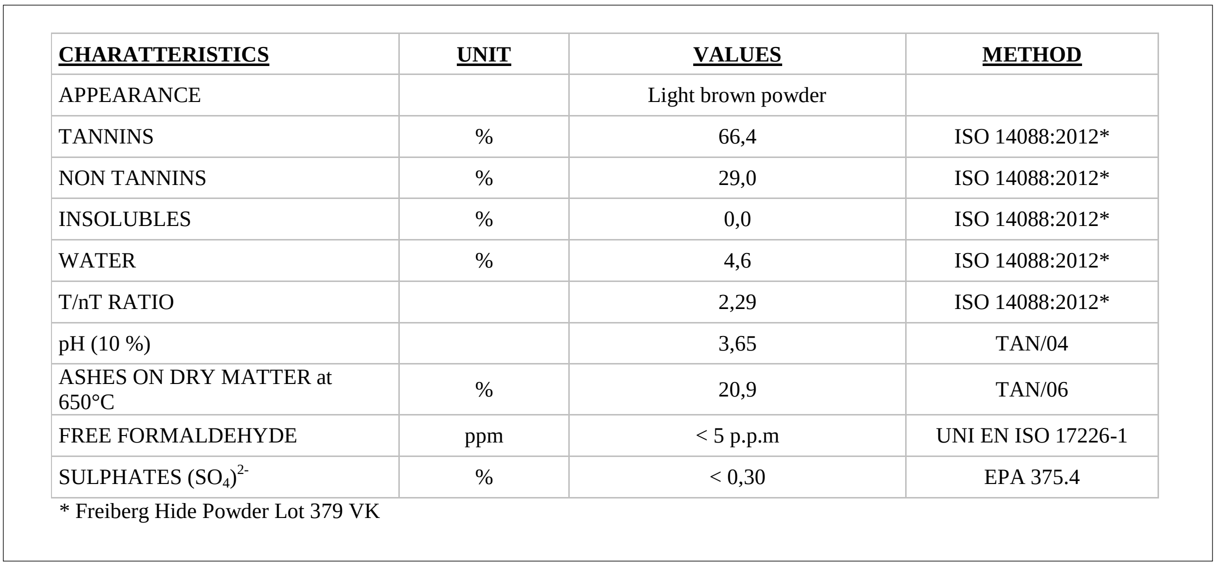


Figure 2 GEDT Production Process.

The final products obtained (**GEDT**) has self-tanning properties on pickled pelt and it shows the following properties:

- 100% soluble
- Near to white colour (light beige)
- Good light fastness
- Good heat fastness
- Excellent penetration
- Medium softness
- 12-15% powder required for **Wet white** pretannage → Shrinkage temperature 68-70°C
- 35-40% powder required for **Full Tannage** → Shrinkage temperature 75-80°C
- Leather like appearance of both wet white and full tannage
- Easy to wet back
- Good dewatering on sammying
- High increase in thickness
- Easy shaving
- Sensitive to iron ions (black coloration)
- High anionic charge (good dye shades but difficult to fix)

The analytical values of the product in powder form obtained by spray drying are listed in Figure 3.



CHARATTERISTICS	**UNIT**	**VALUES**	**METHOD**
APPEARANCE		Light brown powder	
TANNINS	%	66,4	ISO 14088:2012*
NON TANNINS	%	29,0	ISO 14088:2012*
INSOLUBLES	%	0,0	ISO 14088:2012*
WATER	%	4,6	ISO 14088:2012*
T/nT RATIO		2,29	ISO 14088:2012*
pH (10 %)		3,65	TAN/04
ASHES ON DRY MATTER at 650°C	%	20,9	TAN/06
FREE FORMALDEHYDE	ppm	< 5 p.p.m	UNI EN ISO 17226-1
SULPHATES $(SO_4)^{2-}$	%	< 0,30	EPA 375.4

* Freiberg Hide Powder Lot 379 VK

Figure 3 Analytical values of GEDT.

With this tanning material it is possible to make tannage in two ways:

a) Pretannage to obtain a wet white.
b) Full tannage with **GEDT.**

a) Pretannage to obtain a wet white

12-15% of **GEDT** on limed weight is necessary to stabilise a bovine hide. A shrinkage temperature of 68-70°C is obtained. The hides are full and flat with a light brown colour (Figure 4) which becomes ivory white on drying (Figure 5). No pretannage is required.

Figure 4 Pretanned GEDT hide.

Figure 5 GEDT natural crust.

This stabilised hide can be sammed and shaved with regular chromed tannery machines. The dewatering is excellent as well as the shaving. Being very sensitive to iron **GEDT** leathers may get black iron spots which can subsequently be removed during washing with sequestering agents. Opposite to conventional aldehyde pretannages **GEDT** has a leather look after drying and it wets back very easily.

After shaving the character of the leather can be modified in retannage in order to obtain a very wide range of articles.

b) Full tannage with GEDT

Leathers can be fully tanned with **GEDT** using any conventional vegetable tanning system: rapid, semi-rapid or in pits. Around 35-40% material is required on limed weight without any pretannage. After tannage the leather can be shaved, dyed and fatliquored. No retanning is required.

Cationic ester in combination with GEDT

The leathers obtained by pretanning and or retanning with **GEDT** are very pleasant, full and round but the tannage is very anionic therefore as in most metal free systems the leathers have poor reactivity towards common dyes and fatliquors. This means that it is difficult to fix anionic chemicals and floats are not well exhausted.

Two techniques were follow to improve the very poor reactivity of the leathers:

a) Partial recycling of pretanning liquors to improve fixation of tannins.
b) Incorporation of a **C**ationic **E**ster **(CE)** in pickling and in retannage to improve dyeability.

a) Partial recycling of the pretannage floats

At the end of wet white pretannage and main tannage the final floats which are high in COD values, due to unfixed tannins, can be recycled just to do a pretannage of the following batch. In this way the residual tannins are nearly completely fixed with a high reduction of unfixed tanning to the drain. After this "colouring" the liquid is drained to the effluent plant with very low COD values and a new float is prepared for the main pretannage / tannage (Figure 6).

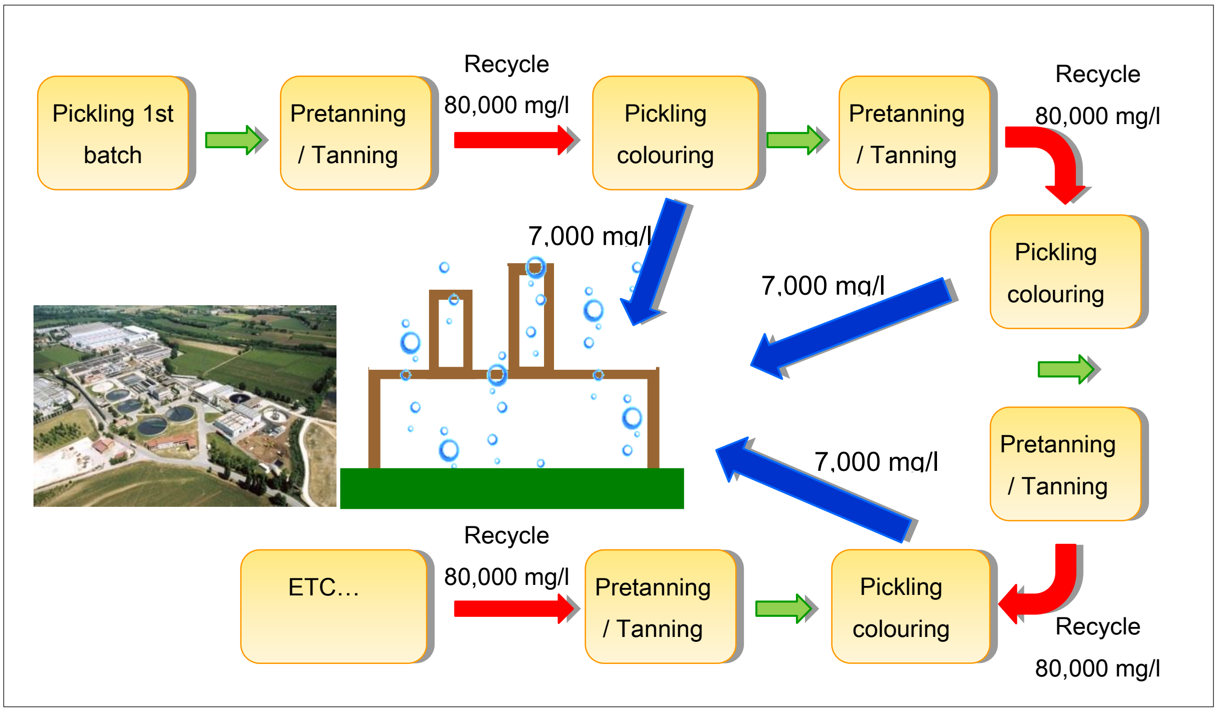


Figure 6 Pretannage / tannage with GEDT with recycling of floats.

b) Incorporation of a cationic ester in GEDT system

In order to increase reactivity and fixation of the anionic chemicals a cationic ester (Figure 7) was used to incorporate cationic charges and increase the isoelectric point of the leather and thus its reactivity.

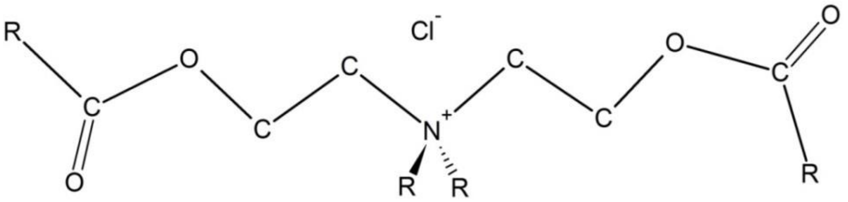


Figure 7 Basic structure of cationic ester.

The collagen structure which is made of cationic and anionic groups in a balanced way (Figure 8), suffers a strong "anionicity" due the the anionic charges incorporated with tanning materials, dyes and fatliquors (Figure 9). For this reason it was studied a cationic ester that adds cationic charges to bring back the number of anionic / cationic groups to a more balanced level (Figure 10).

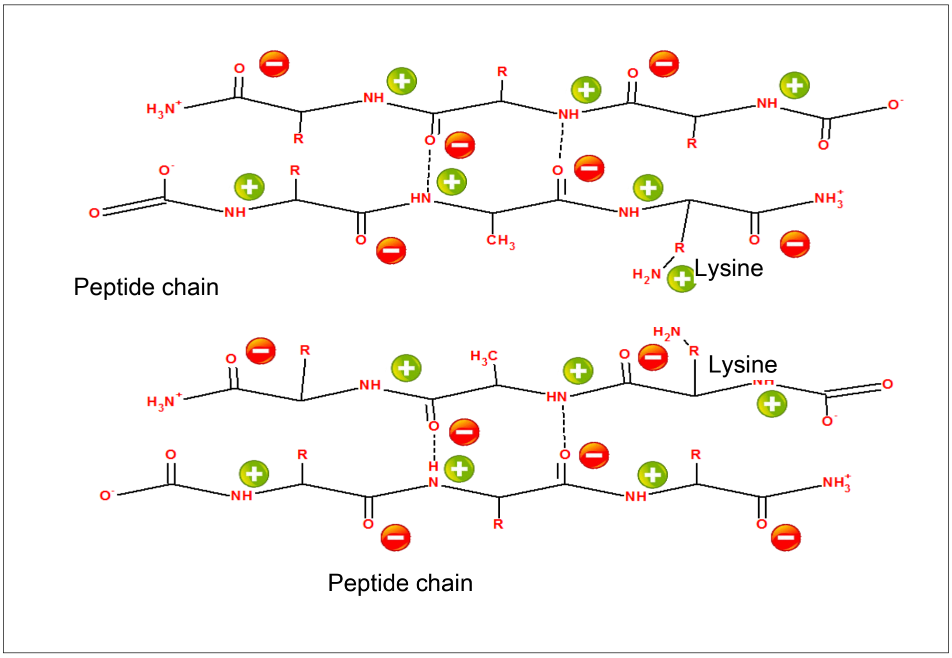


Figure 8 Collagen polypeptide chains.

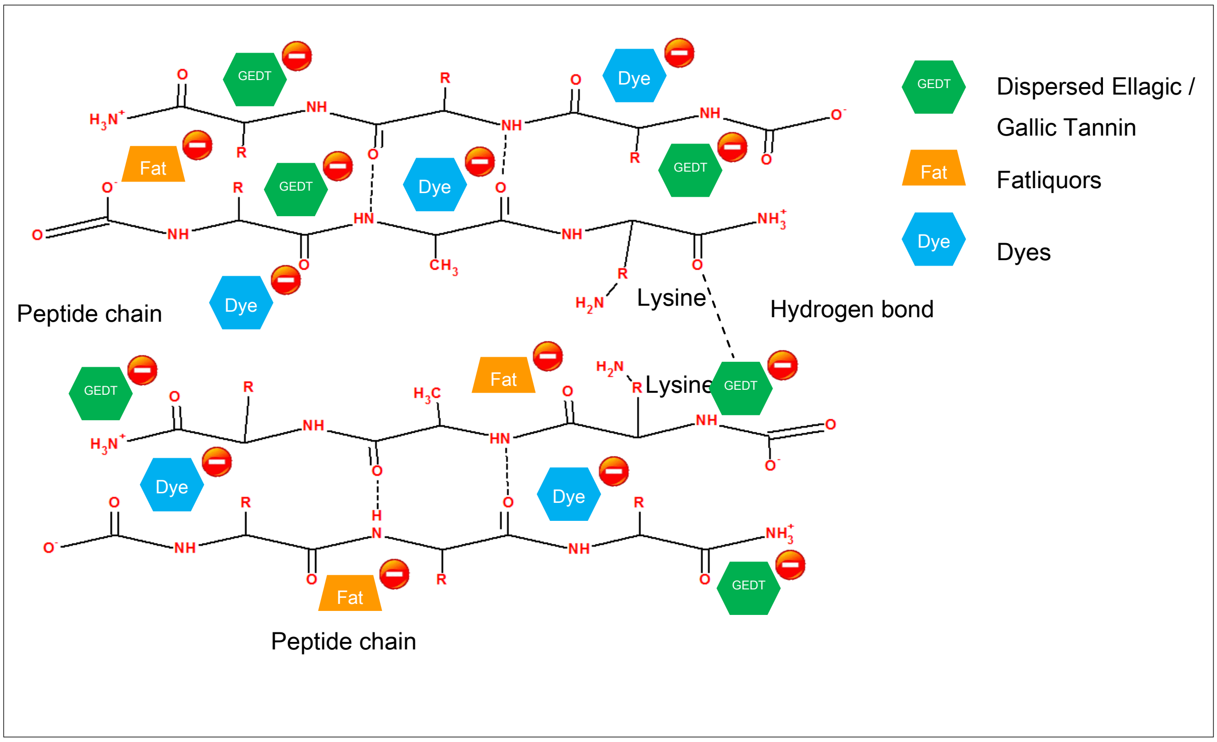


Figure 9 Chrome free GEDT crust.

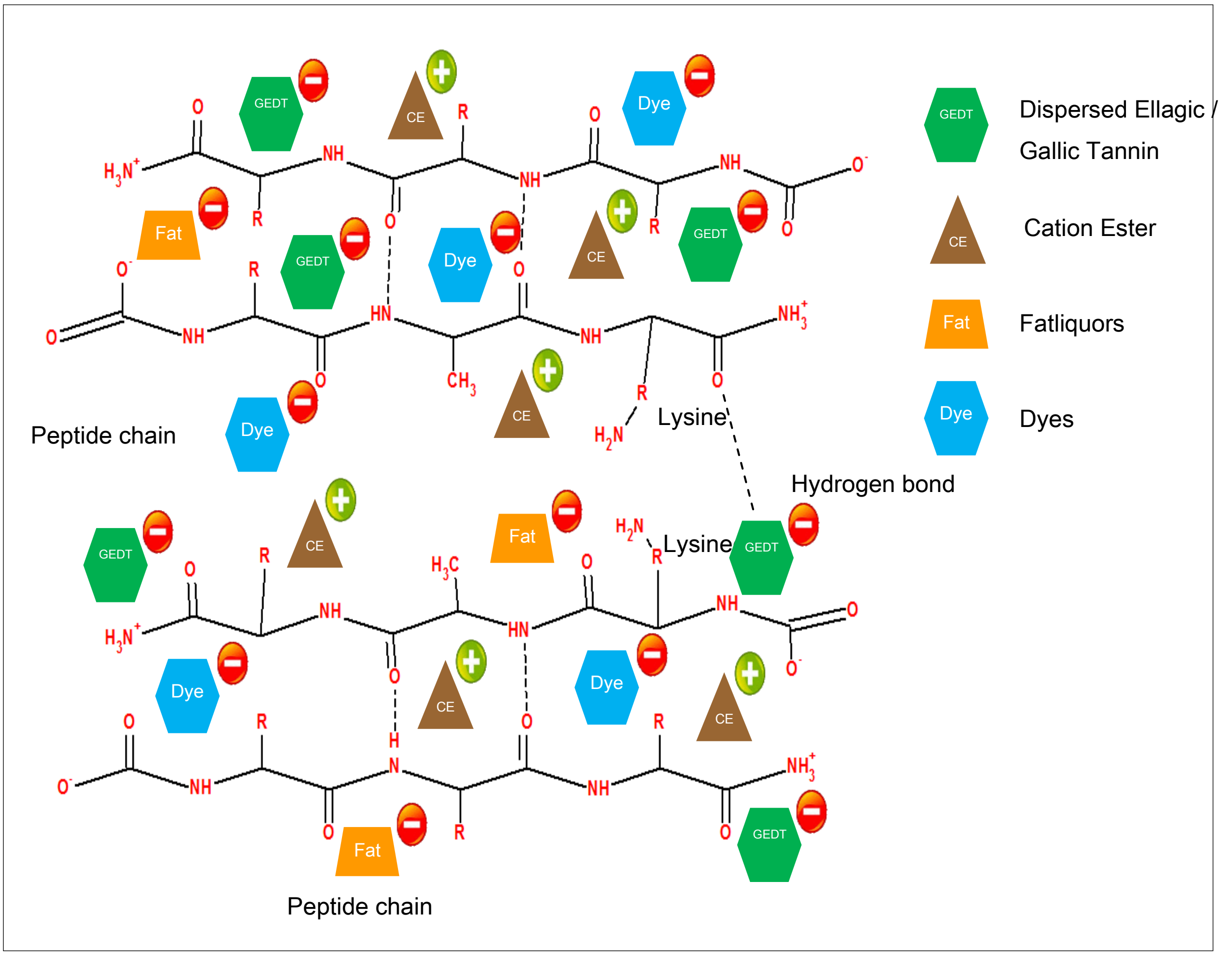


Figure 10 GEDT + CE crust.

2. RESULTS AND DISCUSSION

The various leathers obtained with the **GEDT** tannage in combination with **CE** were evaluated in comparison with conventional Glutaraldehyde / Tara / Syntan leathers in term of shrinkage temperature, dye fixation, exhaustion of tannins by recycling the pretannage float, physical properties of the leathers.

Shrinkage temperature

Shrinkage temperatures obtained with GEDT tannage are between 68 and 85 °C (Figure 11).

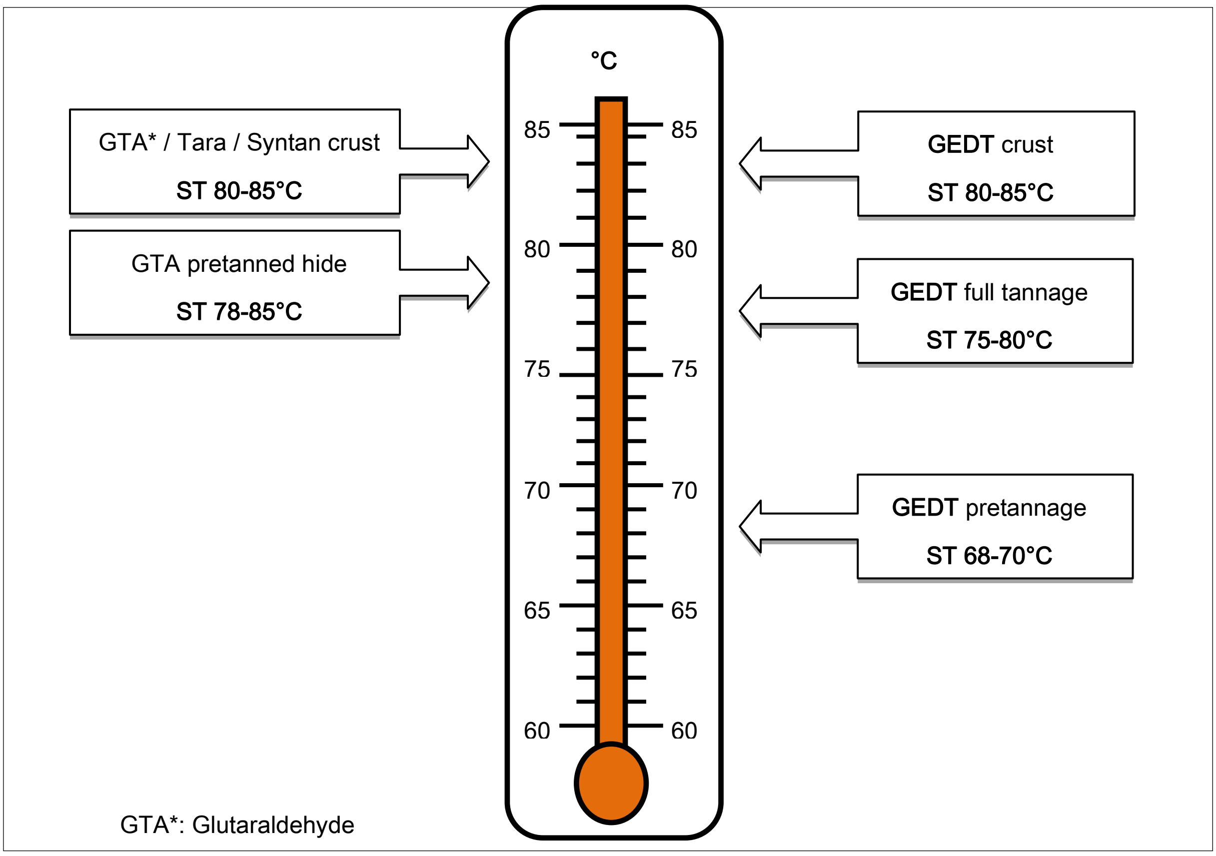


Figure 11 Shrinkage temperature of different pretanning and tanning with GEDT.

Dye fixation

By the incorporation of the Cationic Ester (**CE**) further to the improvement of the exhaustion of tanning materials, dyes and fatliquors there is a considerable positive effect on dye shades (Figure 12).

Figure 12 Influence of cationic ester on dyeing.

Exhaustion of tannins by recycling the pretannage float

Spent liquors of **GEDT** pretannage and tannage can be recycled for a pretannage of the following batches obtaining a further exhaustion of up to 88% which brings the total uptake of tannins to 97% of the amount offered (Figure 13).

	Normal pretannage float with GEDT	**Pretannage float after recovery in "colouring"**	**Reduction**
Density	11.4 Bè	8.4 Bè	-88%
% Tannins	2.4%	0.3%	
% of non tannins	9.8%	8.1%	
T/nT ratio	0.24	0.04	
Ash on dry matter	66.7%	92.7%	
COD value (ppm)	74,800 ppm	21,000 ppm	-72%

Figure 13 Spent liquors of GEDT pretannage and tannage can be recycled for a pretannage

Physical properties of the leathers

Physical properties obtained in the **GEDT + CE** crust are in line with conventional aldehyde /syntan tara / systems regarding tensile strength. Tear values were found slightly higher (Figure 14).

	GEDT + CE crust	**Conventional Glutaraldehyde / Tara / Syntan crust**
Tensile strength (N)	62	62,2
Tear strength (N)	212	177
Grain looseness (1-5)	4.5	4.5
Light fastness (grey scale)	4.0-4.5	3.5-4.0
Heat fastness 120°C 24h (grey scale)	4.5	3.5
Softness (softmeter)	3.2	3.6
Fogging (gravimetric)	2.8mg	2.8mg

Figure 14 GEDT + CE crust physical properties.

Possible leather range

By varying the retannage and fatliquoring a very wide range of articles can be obtained, such as leather for automotive, furniture, shoe upper (Figure 15).

Figure 15 GEDT + CE leathers permit to obtain a huge range of articles.

Biodegradability of pretanning / tanning effluents:

Biodegradability tests were carried out on the spent liquors of pretanning with the GEDT and after colouring. The test was made in a pilot biological treatment plant with a retention time of 65 days using activated biological sludge from a tannery water treatment plant.

The test shows that spent liquor from pretannage is degraded 70% while the same liquor after colouring is degraded 85%

3. Conclusion

- It is possible to pretan / tan leathers with **GEDT** without the use of aldehydes and / or metals
- Process is simple and assimilated to conventional Vegetable tannin systems.
- It is possible to use cationic esters to improve softness, dyebility and strength properties of conventional veg tanned leathers.
- **GEDT** gives excellent light and heat fastness leathers compared to other FOC techniques.
- Colour of **GEDT** leather in combination with **CE** is very light.
- By recycling the final liquor of **GEDT** tannage for a precolouring of the following batch the residual tanning material can be exhausted to very high levels.
- By a combination of **GEDT** and **CE** very high performing leathers can be obtained.

4. Acknowledgements

A great thanks to all Silvateam's staff who contributed in this project, in particular to Andrea Calleri, Massimo Gotti and Paolo Saccagno.

5. References

1) Stanley G. Shuttleworth L.I.R.I South Africa pag. 181
2) *Gustavson K.H.,* The Chemistry of Tanning Processes*, Academic Press, New York, 1956.*
3) Dr. Yalcin Dikmelik Deri Teknolojisi
4) Van Buren J.P., Robinson W.B., *Formation of complexes between protein and tannic acid.* J. Agric. Food Chem., 1969, 17(4):772–777. DOI: 10.1021/jf60164a003
5) McLaughlin G.D., Theis E.R., Orthmann A.C., *The chemistry of leather manufacture*. J. Phys. Chem., 1946, 50(4):548-587. DOI: 10.1021/j150448a012

IVL O-12

INTELLIGENT REAL TIME LEATHER DEFECT DETECTION SYSTEM USING IMAGE PROCESSING TECHNIQUE

Malathy Jawahar*, N.K. Chandra Babu

Central Leather Research Institute, Adyar, Chennai – 600 020, India,
Email: malathyj@clri.res.in, malathy.jawahar@gmail.com

The inspection of leather quality is very important in assessing the effective cutting value that can be obtained from the leather when used for making leather products. Leather being a natural material, quality of the leather varies due to the inherent variation in the raw material. The price of the skin or leather varies quite considerably with the selection and hence grading is done with diligent care by experienced assorters. However such a manual inspection is highly subjective and varies quite considerably from one assorter to another and often this subjectivity leads to dispute between the buyer and the seller of the leathers. Manual leather defect detection is tedious and subjective and repetitive inspection often results in missing the defects due to fatigue leading to inaccuracy and inconsistency.

To resolve the drawbacks of the manual method, an intelligent automatic leather defect detection using image processing technique is proposed in this paper. In the proposed method, the optimal texture features such as Entropy, Energy, Contrast, Correlation, Cluster Prominence Standard Deviation, Mean, and local homogeneity that discriminate between normal and defective leathers are extracted. The normal and defective leathers are classified using an artificial neural network features. Experimental results on the leather defect image library database suggest that the identification of leather defects can be automated with the application of image processing technique based on feature extraction technique using ANN as Classifier.

Keywords: Leather surface inspection, Leather defect, Image processing technique, Artificial neural network

Introduction

There is a growing awareness regarding the quality of consumer goods. Global market puts higher demand on quality and hence there is an increasing role for quality control in leather production process. As quality of the leather varies because of the inherent variation within the natural raw material, an objective quality assessment plys a vital role in meeting the end user requirements. Assessment of effective cutting value during the product manufacture is done based on the number and location of defects present on the leather substrate. Therefore, price of the leather varies quite considerably with its effective cutting value and hence it is an important exercise that is done with diligent care by experienced assorters. There is no universally accepted grading rules defined based on leather surface defects. Each buyer/seller sets their own grading rules, in grading the leather which is highly subjective and varies quite considerably from one assorter to another and often this subjectivity leads to dispute between the buyer and the seller of the leathers.

Machine vision (Chin and Harlow 1982; Cho et al 2005; Newman and Jain 1995; Perner 1994; Thomas and Rodd 1995) and Computer aided analysis (provides way for automatic surface inspection and identification of leather surface defects. Image Analysis (Kumar and Pang 2004; Wilson et al 1997;Yang et al 2002 and 2004) and Pattern Recognition are the potential areas of research in automated leather surface inspection and assessment. New mathematical algorithms based on image texture has been employed in this study to understand the nature of leather defects captured by the industrial CCD camera images. Texture analysis of the leather images gives an overall perspective of the spatial distribution of pixels. Image texture gives information about the spatial arrangement of intensities in an image. It works similar to the visual perception of human beings and handles uncertainties very effectively. Texture analysis (Haralick et al 1973; Kumar and Shen 2002; Unser and Ade 1984; Tuceryan and Jain 1993) includes collective analysis of local pixel regions, rather than relying upon spatial information from single pixel. This paper presents an intelligent real time leather defect detection system to give quantitative feature description of leather surface images for classification of different leather defects based on texture analysis.

Wavelet Transform

Wavelet transform offers an efficient representation and good visual for images. Wavelet had proved that it is very useful for detection (Kim et al 1999; Tsai and Hsiao 2001; Serdaroglu et al 2006; Strickland and Hahn 1996) and matching applications (Arivazhagan and Ganesan 2003; Choplet et al 2006; Padma and Sukanesh 2011) . Multiresolution analysis is one of the most important features in the wavelet transform. Mallat and (1996) explained the application of repetitive low and high pass filters and it gives the coefficients in four quadrants such as approximation(low low frequency), horizontal (low high frequency), vertical(high low frequency) and diagonal (high high frequency) as shown in Fig.1.

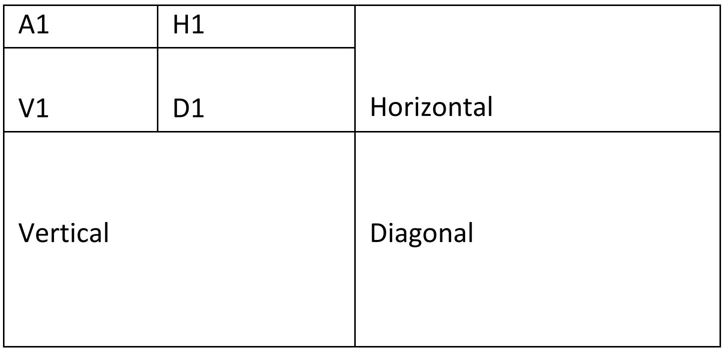


Fig 1: Wavelet Transform Representation

Several bases are available in the wavelet transform. In this study, entropy based method has been used to select wavelets (Patrick et al 2006). For optimal wavelet selection, information extraction criteria and distribution error criteria were used (Leizhang et al 2005). Based on the property of signal /image, wavelet were selected (Ahuja et al 2005). There is no unique technique or parameters to choose the wavelet. Survey on mother wavelet selection method gives the broader view about the wavelet selection method(Rafiee et al 2009). The property of discrete, orthogonality and compact support properties were chosen to narrow down the selection of wavelets into four wavelets out of fifteen wavelets. The four selected wavelets were Haar, Daubechies, Symlet and Coiflet. Level of decomposition gives enhanced conception of an image. Based on the energy of the sub bands, the level of decomposition is stopped. Two level decomposition was done and further decomposition was not required because the energy content became zero and hence two level decomposition was carried out in this present study as depicted in Fig.2.

Original Image	Decomposed Image
	
	

Fig 2: Defective and non-defective leather samples with Wavelet decomposition

Experimental

Intelligent real time leather defect detection system is designed in such a way to automate the leather surface inspection for identifying the surface defects. The leather imaging setup consists of a feed roller, a delivery roller, CCD camera attached to scanning carriage. As the leather is being conveyed by the rollers, the scanning carriage moves the CCD camera horizontally and in each row 10 leather images are captured. Leather being natural material, the number of rows vary from 10 to 12 rows. The size of each acquired leather image is around 1600 X 1200 pixels. The database contains the images of the representative set of defective and non-defective leather samples. The stored the leather sample images are used for the training and testing to classify defective and good or non-defective leather.

RESULTS AND DISCUSSION

MATLAB R2012, version Image Processing Toolbox was utilised in this analysis. Using the leather surface imaging setup, the whole leather surface image was captured. These images aid real time monitoring of the defective and non-defective leather regions. Fig. 3 shows the work flow diagram for identification of the leather surface defects. To speed up the computation time, the captured leather images were converted to greyscale and transformed to wavelet domain.

Wavelet analysis of leather images provides vital information about textural features reflecting the coarseness, smoothness, contrast, and randomness of pixel distribution. Statistical measurements such as higher order moments and correlation represent similarity of pixels. The feature set comprising of Mean, Standard Deviation(SD) , Skewness, Kutosis, Homogeniety, Inverse Difference Momentum (IDM), Mean Energy, Mean Absolute Deviation (MAD), Co-variance (CV), Inter Quartile Range(IQR), Angular Radial Partitioning (ARP) Transform Domain Features act as predictor coefficients to identify the leather surface defects. Figures 4 and 5 show the discriminative ability of these extracted feature set. The good leather surface has a very smooth texture and was highly homogeneous. This was quite evident with very low variance, in SD, MAD, CV and IQR. Similarly randomness was very less with lower entropy values. Defects such as bacterial infection, fungal attack, grain damage, pox mark, lime blast etc., showed porous patches with rough and coarse texture. Hence, high SD, MAD and CV values, and randomness with high Entropy value. Defects such as Chrome Patch, dye patch etc., visually seem to be smooth texture with variable intensity patches. The feature values reflected these defects with higher mean intensity, Probability distribution (kurtosis), Skewness values and Homogeneity.

The extracted discriminant texture features values were given as input to the Artificial Neural Network (ANN) to classify the leather surface images as defective and non-defective class. Fig. 6 shows ANN training plot. Initially with known input-output pair, the network was trained for 10000 number of epochs. The network converged after 8552 iterations (epochs) with error threshold of 0.118 thus resulted in the good accuracy for the test data. After training, network was used to identify the defective and non-defective regions of the unknown whole leather images. The classification accuracy was above 90%, with chrome and dye patch defects having close margin.

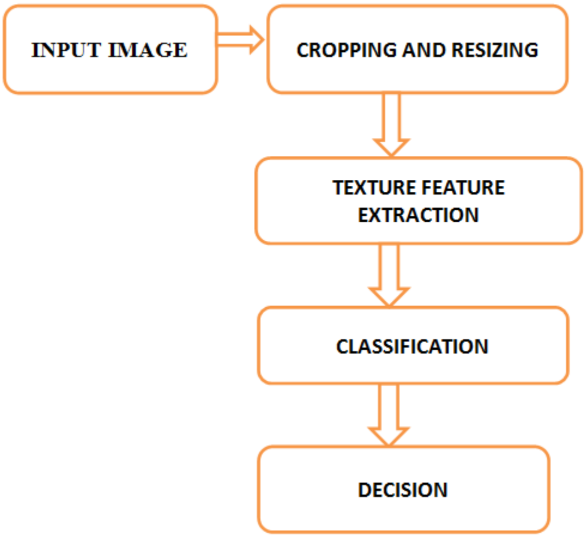


Fig. 3 Work flow diagram for leather surface defect identification

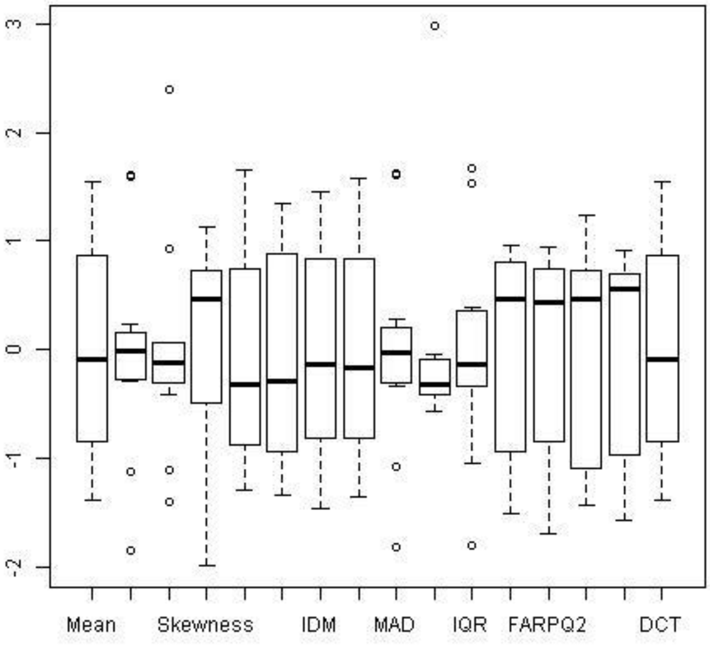


Fig.4 Box plot of the feature set

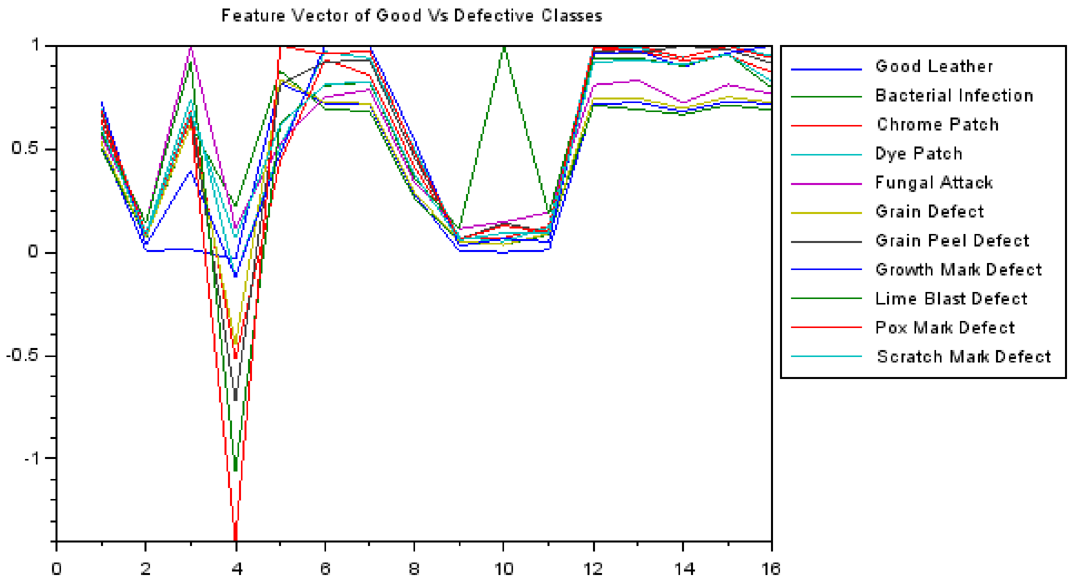


Fig.5 Feature vector plot of Good vs various types of leather defects

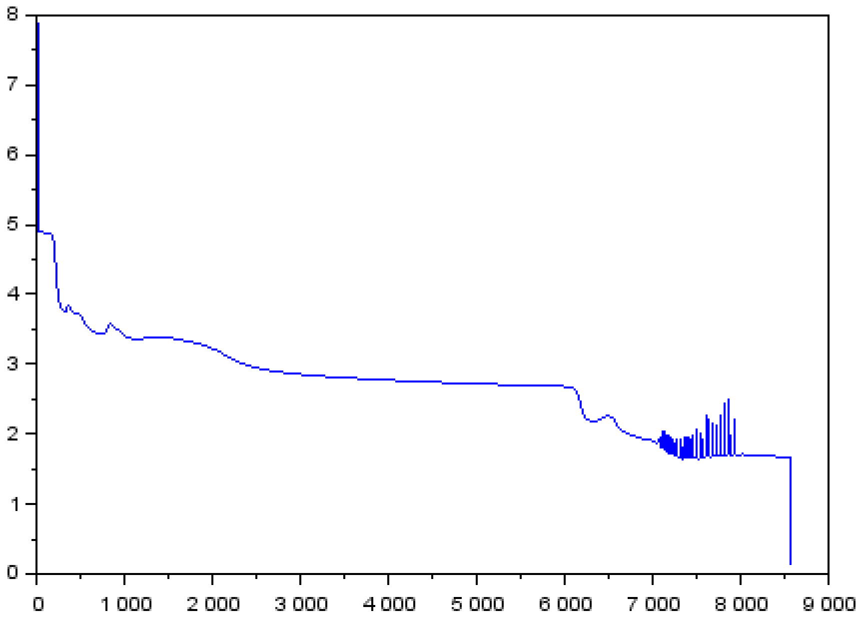


Fig. 6 ANN training plot

CONCLUSION

This paper shows the application of the Machine vision and Computer aided analysis of leather surface images to identify and classify the defects. Texture analysis based on spatial and frequency domain features such as Mean, Standard Deviation(SD) , Skewness, Kutosis, Homogeniety, Inverse Difference Momentum (IDM), Mean Energy, Mean Absolute Deviation (MAD), Co-variance (CV), Inter Quartile Range(IQR), Angular Radial Partitioning (ARP) was used to characterize the various types of defects. This feature set showed good discriminative ability and gave better results in detection of defects for leather inspection. Neural network was used to classify the defects and has shown 90% classification accuracy.

Thus present approach using image processing algorithm for identification of leather defects and neural networks appears promising for automatic inspection and has shown the technical feasibility of an automatic intelligent real time leather defect detection inspection system. The system inspects all the areas of the leather avoiding the problems of human fatigue, missing of defects etc., Automated leather defect inspection system delivers accurate results in identifying the surface defects providing consistent and quality inspection thereby increasing the productivity and reliability of assessment.

ACKNOWLEDGMENT

The authors acknowledge the financial support from CSIR, New Delhi under the Supra Institutional Project S&T Revolution in Leather with a Green Touch (STRAIT) (CSIR-CLRI Communication No. 1229). This research work is carried out as part of PhD registered in Anna University, Chennai, INDIA.

REFERENCES

1. Ahuja, N., Lertrattanapanich,S. and Bose, N. K. , Properties determining choice of mother wavelet, *IEEE Proceedings Vision, Image and Signal Processing*, 2005, **152(5)** 659 -664.
2. Arivazhagan S, Ganesan L, Texture classification using wavelet transform, *Pattern Recognition Letters*, 2003, **24**, 1513–1521.
3. Chin R. T, Harlow C A, Automated visual inspection: A survey, *IEEE Trans. Pattern Anal. Mach. Intell.*, 1982, **4(6)**, 557–573.
4. Cho C S, Chung B M, Park M J, Development of real-time vision-based fabric inspection system, *IEEE Trans. Ind. Electron.*, 2005, **52(4)**, 1073–1079.
5. Choplet S, Patnaik L M, Jaganathan N R, Classification of magnetic resonance brain images using wavelets as input to support vector machine and neural network, *Biomed. Signal Process Control*, 2006, **1(1)**, 86–92.
6. Haralick R M, Shanmugam K, Dinstein I, Texture features for image classification, *IEEE Trans. System Man Cyberna,* 1973, **8(6)**, 610–621.
7. Hepplewhite L, Stonham T J, Surface inspection using texture segmentation, *IEE Colloq. Texture Classification: Theory Appl.*, 1994, 589–592.
8. Kim S, Lee M H, Woo K B, Wavelet analysis to defects detection in weaving processes, *Proc. IEEE Int. Symp. Ind. Electron.*, 1999, **3**, 1406–1409.
9. Kumar, Shen H C, Texture inspection for defects using neural networks and support vector machines, *Proc. ICIP, Rochester, NY*, 2002, 353–356.
10. Kumar, Pang G, Defect detection system for quality assurance using automated visual inspection, *U.S. Patent,* 2004, **6**, 753 965.
11. Lei Zhang, Paul Bao, and Xiaolin Wu, Multiscale LMMSE-Based Image Denoising With Optimal Wavelet Selection, *IEEE Transactions on Circuits and Systems for Video Technology*, 2005, **1(4),** 469 - 481.
12. Mallat S, Wavelet for a vision, *Proceedings of the IEEE*, 1996, **84**, 604-614.
13. Rafiee J., Tse P.W., Harifi A., Sadeghi M.H., A novel technique for selecting mother wavelet function using an intelligent fault diagnosis system, *Expert Systems with Applications*, 2009, **36**, 4862–487.
14. Nugi W K, M salman Leong et al 'Wavelet Analysis: Mother Wavelet Selection Method' *Applied Mechanics and Materials*, 2013Vol. 393, 953-958.
15. Newman T S, Jain A K, A survey of automated visual inspection, *Comput. Vis. Image Underst*., 61, 1995, **2**, 231–262.
16. Padma A, Sukanesh R, A wavelet based automatic segmentation of brain tumor in CT images using optimal statistical texture features, *Int. J. Image Process*., 2011, **5(5)**, 552–563.

17. Padma A, Sukanesh R, Texture feature based analysis of segmenting soft tissues from brain CT images using BAM-type artificial neural network, *J. Inf. Eng. Appl.*, 2011, **1(4)**, 34–43.
18. Patrick P C Tsui, Otman A Basir, Wavelet basis selection and feature extraction for shift invariant ultrasound foreign body classification, *Ultrasonics,* 2006, **45**, 1-14.
19. Perner P, A knowledge-based image-inspection system for automatic defect recognition, classification, and process diagnosis, *Mach. Vis.Appl*., 1994, **7**(**3)**, 135–147.
20. Serdaroglu A, Ertuzun, Ercil A, Defect detection in textile fabric images using wavelet transforms and independent component analysis, *Pattern Recognit. Image Anal*., 2006, **16(1)**, 61–64.
21. Strickland R N, Hahn H I, Wavelet transforms for detecting microcalcications in mammograms, *IEEE Trans. Med. Imaging,* 1996, **15(2)**, 218-229.
22. Thomas D H, Rodd M G, Holt J D, Neill C J, Realtime industrial inspection: A review, *Real-Time Imaging*, 1995, **1(2),** 139–158.
23. Tsai D M, Hsiao B, Automatic surface inspection using wavelet reconstruction, *Pattern Recognit.*, 2001, **34(6**), 1285–1305.
24. Tuceryan M, Jain A K, Texture analysis, *Handbook of Pattern Recognition and Computer Vision, Chan C H, Pau L F, Wang P S P, Eds. Singapore: World Scientific*, 1993, **2**, 235–276.
25. Unser M, Ade F, Feature extraction and decision procedure for automated inspection of textured materials, *Pattern Recognit. Lett*., 1984, **2(3)**, 181–191.
26. Wilson D, Greig A, Gilby J, Smith R, Using uncertainty techniques to aid defect classification in an automated visual inspection system, *IEE Colloq. Ind. Inspection*, 1997, 2/1–2/10.
27. Yang X Z, Pang G, Yung N, Discriminative fabric defect detection using adaptive wavelet, *Opt. Eng*., 2002, **41(12**), 3116–3126.
28. Yang X, Pang G, Yung N, Discriminative training approaches to fabric defect classification based on wavelet transform, *Pattern Recognition*, 2004, **37(5)**, 889–899.

IVL O-13

ANALYSIS OF CHARACTERISTIC ODOR COMPOUNDS IN LEATHER BY GC-MS AND GC-OLFACTOMETRY

Hirohiko Washiya*, Osamu Harada, Masaru Mori

Technical Support Center for Leather Industries, Hyogo Prefectural Institute of Technology, 3 Nozato, Himeji, Hyogo 670-0811, Japan Email:washiya@hyogo-kg.jp

The odor component of leather is a mixture of various volatile compounds. Odor analysis of leather has been performed mainly by gas chromatography-mass spectrometry (GC-MS). Each of the peaks in the chromatogram represents an individual compound that was separated from a sample mixture. However, it is unknown whether each peak represents an odor-active compound. For the odor analysis of foods and flavor, gas chromatography-olfactometry (GC-O) is used. GC-O involves the use of human assessors as sensitive detectors for odor-active compounds. The sensitive detector, the human "nose", enables the recognition of substances that cannot be identified using other methods of analysis. In this study, the volatile compounds in leather were extracted using a solid-phase microextraction fiber and then identified using GC-MS and GC-O. The results showed that more than 20 major volatile compounds were identified by GC-MS. Among them, hexanal, heptanal, octanal, nonanal, heptanol, octanol, 2-ethoxyethanol, and 2-buthoxyethanol were the main compounds. Aldehydes such as octanal and alcohols such as octanol were characterized by GC-O. In contrast, solvents such as 2-ethoxyethanol were not characterized by GC-O.

Keywords: solid-phase microextraction, gas chromatography-mass spectrometry, gas chromatography-olfactometry, odor

1. INTRODUCTION

The protein collagen, which is the main component of leather, is odorless. The odor components are added through various processes. In leather manufacture, various compounds, each with its own odor, are used. These complex odors constitute the odor of the leather. Tannin gives off a unique odor, while the compounds used for finishing have a solvent odor. In previous studies, the causative substances of the leather odor have been investigated[1]. Leather odor analysis has been performed mainly by gas chromatography-mass spectrometry (GC-MS). Each of the peaks in the chromatogram represents an individual compound that was separated from a sample mixture. However, it is unknown whether each peak represents an odor-active compound. In order to determine the components of the odor, it is necessary to sniff the GC effluent. In 1964, Fuller, Steltenkamp, and Tisserand published the first description of a GC method modified for this purpose[2]. For the odor analysis of foods and flavors, gas chromatography- olfactometry (GC-O) is generally used. GC-O involves the use of human assessors as sensitive detectors for odor-active compounds. In this study, the volatile compounds in leather were extracted using a solid-phase microextraction (SPME) fiber and identified using GC-MS and GC-O for determining the characteristic odor-active compounds in leather.

2. MATERIAL AND METHODS

2.1 Materials

Ten finished samples were selected from the leathers exhibited at the Hyogo New Leather Contest 2015 held in Hyogo Prefecture, Japan. Before analysis, all the samples were maintained at a temperature of 20 °C and a relative humidity of 65% for 2 or more days.

2.2 Extraction

For sampling the volatile compounds in leather, a SUPELCO DVB/Carboxen/PDMS fiber (50/30 µm thickness) was selected from the four types of SPME fibers. Before sampling, the SPME fiber was reconditioned, and then, it was exposed for 10 min to the headspace of a 0.5 g sample in a 20 mL headspace vial at 70 ℃. After sampling, the SPME fiber was placed in the injection port of the GC-MS system.

2.3 GC-MS analysis

The schematic of GC-MS and GC-O is shown Fig.1. The GC-MS analysis was performed using PerkinElmer AutoSystem XL with a PerkinElmer Turbomass mass spectrometer.

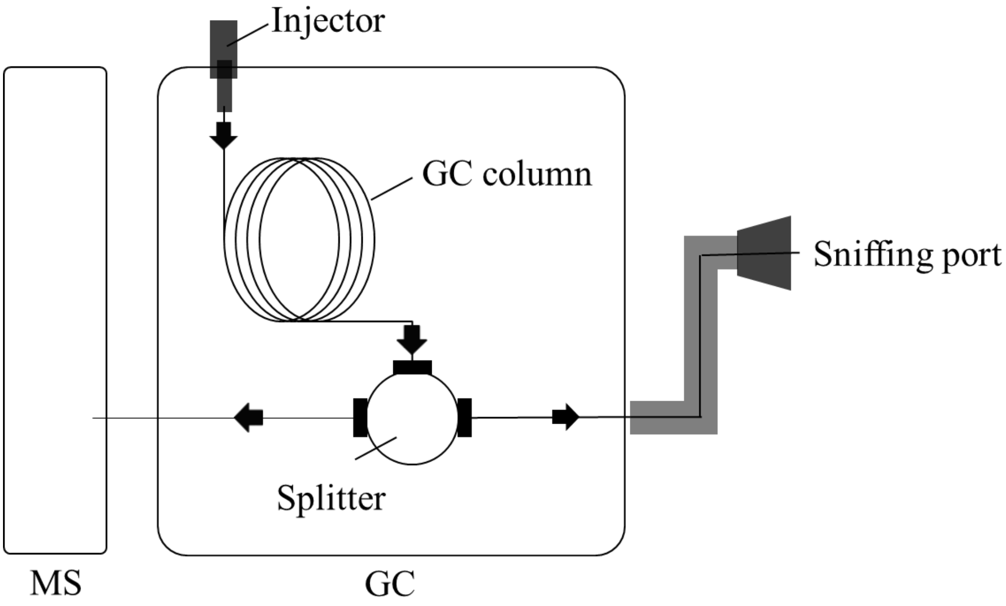


Fig. 1. Schematic of GC-MS and GC-O

The samples were analyzed using a fused-silica capillary column, DB-WAX (30 m x 0.25 mm, 0.25 µm film thickness, GL Sciences Inc.). The flow of the carrier gas (helium) was controlled and was set at 1.0 ml/min. The GC oven was temperature programmed from 40 °C to 230 °C at the rate of 10 °C /min. The MS transfer line was 230 °C, and the mass spectrometer was operated in electron impact (EI) ionization mode (70 eV) with a mass range 50-400 m/z.

2.4 GC-O analysis

GC-O analysis was performed on a GL Sciences Inc. OP275 instrument. The GC eluent from the capillary column was split in 1:3 (v/v) ratio between the mass spectrometer and the sniffing port. The samples were injected into the GC system in splitless mode. The GC conditions, transfer line temperature, and carrier gas were the same as those described above. The odor identity was decided at the sniffing port.

3. RESULTS AND DISCUSSION

3.1 Volatile compounds

A representative total ion chromatogram (TIC) of finished leather is shown in Fig. 2. The compounds were identified using the NIST (National Institute of Standards and Technology) libraries. More than 20 volatile compounds were detected. The volatile compounds and their corresponding peak numbers are listed in Table 1. The largest peak, peak 11, corresponds to 2-butoxyethanol, which is a glycol ether.

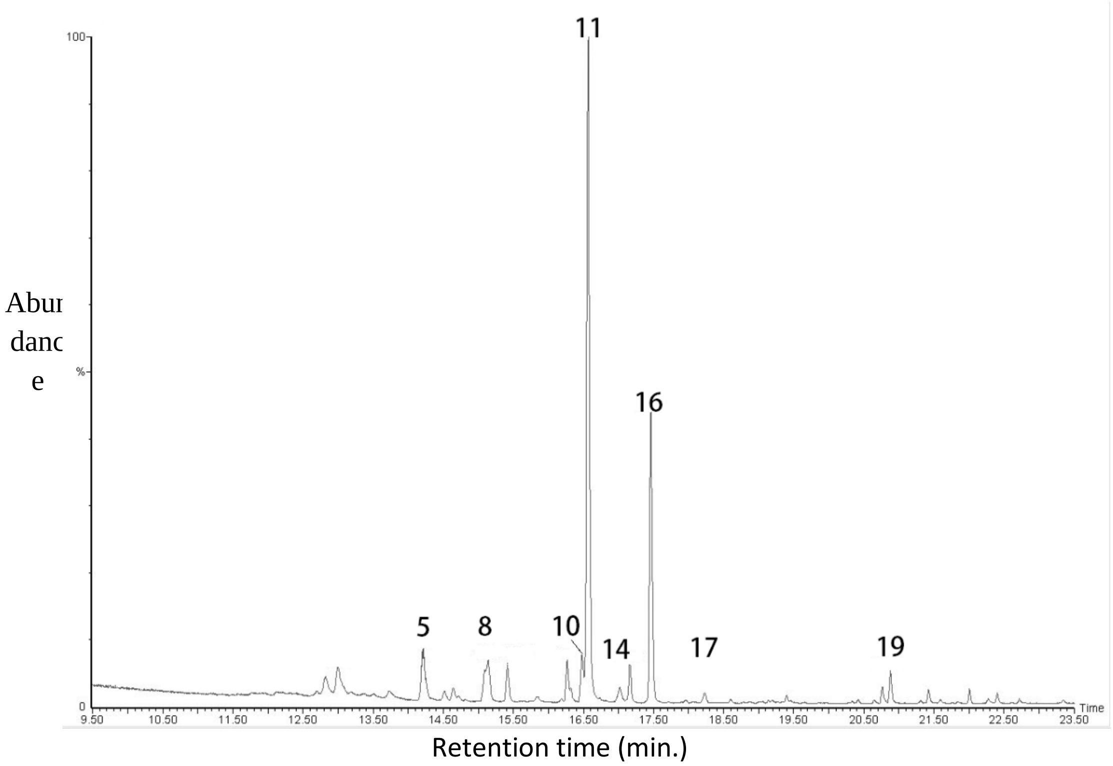


Fig. 2. A representative total ion chromatogram (TIC) of finished leather

It is a colorless liquid, which is miscible in water and soluble in most organic solvents. In the leather industry, 2-butoxyethanol is widely used as a lacquer for spraying. Peak 5 represents 2-ethoxyethanol, which has similar properties as those of 2-butoxyethanol. Peak 16 represents 2-ethylhexanol, which is used as bis (2-ethylhexyl) phthalate used as a PVC plasticizer. These three compounds are detected and characterized from lacquer finished leather. Peak 8 and peak 10 correspond to octanal and nonanal, respectively, which are lower aldehydes. The hydrocarbon chains of lipids and fatliquoring agents form aldehydes when oxidized. Peak 14 and peak 17 represent heptanol and octanol, respectively. Octanol is used in organic synthetic solvents, plasticizers, and surfactants. These alcohols are components of the finishing agents for leather. The main volatiles detected from the 10 finished leathers are shown in Table 1. A total of 19 compounds were detected in most of the samples. Although many types of volatile compounds are emitted from finished leathers, they are relatively low molecular weight components, such as alcohols and aldehydes.

Table 1. Volatile compounds in finished leather

No.	Ret. Time(min.)	Compounds	No.	Ret. Time(min.)	Compounds
1	12.07	Hexanal	11	16.56	2-Buthoxyethanol
2	12.82	1-Methoxy-2-propanol	12	16.89	3-Methoxy-3-methyl-1-butanol
3	13.00	3,4-Dimethyl-1-pentanol	13	16.90	2-Octenal
4	13.67	Heptanal	14	17.01	Heptanol
5	14.16	2-Ethoxyethanol	15	17.46	2-Propyl-1-pentanol
6	14.28	2-Pentylfuran	16	17.48	2-Ethylhexanol
7	15.06	2-(2-Methoxypropoxy)propan-1-ol	17	18.23	Octanol
8	15.11	Octanal	18	20.76	2-Methyl-1-undecanol
9	15.24	1-(2-Methoxypropoxy)propan-2-ol	19	20.88	Diethylene glycol monobutyl ether
10	16.43	Nonanal			

3.2 Odor-active compounds

In order to identify the odor-active compounds in leathers, the finished leathers were analyzed by GC-O. The detected odor-active compounds are shown in Table 2, listed in the order of their elution time from the GC column. Five odor-active compounds were detected in the finished leathers. Heptanal gave off a fruity odor, while nonanal and octanal gave off a green odor. Aliphatic aldehydes such as heptanal, ocatanal, and nonanal are the important fragrance molecules that cause the citrus scent. In addition, the odor quality changes with the concentration of the odorous compounds. Oxidized oil odor emanated from heptanol and octanol. As with the case of the aldehydes, it is considered that the odor quality changes depending on the concentration of the alcohol. Hence, aldehydes such as octanal and alcohols such as octanol are the characteristic odor-active compounds in the finished leathers. 2-Butoxyethanol is the most abundant component detected by GC-MS analysis; however, it was not detected at the sniffing port. 2-Ethoxyethanol and 2-ethylhexanol were not detected as well. Each odorant has its own odor threshold, which is the lowest concentration of a certain odor compound perceivable by the human nose. The higher the odor threshold, the weaker is the odor. Since the above-mentioned aldehydes have a low odor threshold, the odor can be detected even at low concentrations. Conversely, 2-butoxyethanol has a high odor threshold and hence is not detected by the human nose. Therefore, compounds with a high odor threshold are not the characteristic odor-active compounds in finished leather.

Table 2. Odor-active compounds in finished leather

No.	Compounds	Odor	No.	Compounds	Odor
4	Heptanal	fruity	14	Heptanol	oily
8	Octanal	green	17	Octanol	oily
10	Nonanal	green			

4. CONCLUSION

The odor-active compounds in finished leathers were analyzed by GC-MS and GC-O. A total of 19 compounds were detected in most of the samples by the GC-MS analysis. Five odor-active compounds were detected by GC-MS and GC-O analyses. Aldehydes such as octanal and alcohols such as octanol were the characteristic odor compounds in the finished leather, whereas solvents such as 2-buthoxyethanol were not.

5. ACKNOWLEDGEMENTS

We would like to thank Editage (www.editage.jp) for English language editing.

6. REFERENCES

1. K. Sato, A. Okumura, T. Inatsugi, S. Dohshi, E. Fujita, and Y. Tsunoda, Hikakukagaku, 2006, **52**, 59-67.
2. Fuller, G. H., Steltenkamp, R., Tisserand, G. A., Annals N. Y. Acad. Sci., 1964, **116**, 711-724.

IVL O-14

METHOD FOR DETERMINING THE OPTIMIZED EXHAUSTION OF FATLIQUORS TO MINIMIZE THE ETP-INFLOW

Dirick von Behr*, Sjoerd van Driesten

Smit&zoon, Nijverheidslaan 48, 1382 LK, Weesp
**Email: dirick.vonbehr@smitzoon.com, sjoerd.vandriesten@smitzoon.com*

The proposed amendment of the German regulation for the treatment of tannery wastewaters (ATV-DVWK-M774-proposal 2015) emphasizes the minimization of the pollution burden before treatment (inflow). Current regulations are directed towards setting limits to what may leave an ETP (outflow). The new provisions, on the other hand, demand that a verifiable reduction of the polluting load is realized before the water enters the treatment system. An absolute decrease at the level of individual components requires the measurement of these components for a starting point.

This paper discusses the ways of expressing the exhaustion of a selection of fatliquors on chrome and chrome-free leathers. Each product has a specific affinity to the tanned hide and an individual environmental imprint. This specificity can be used for targeted reduction of the inflowing pollution burden.

The findings of the study can act as a starting point for setting up an own methodology and a detailed level of reporting for all who need to understand a fatliquor's true affinity towards the leather and those who endeavor to minimize the environmental impact of their processing.

Keywords: exhaustion, environment, fatliquor, chrome, FOC, ETP.

1. Introduction

The constitution of untreated effluent float depends on composition, quantities and manufacturing of the chemicals used during the upstream process. Effluent constitution depends on the type of processing in the tannery: the effluents of wet blue producers are different to those of tanneries that process from raw to finish, which in turn are of other constitution than the floats from producers that work from tanned stock and limit themselves to crusting and finishing.

Liming and tanning yield effluents of more or less known composition, but the inclusion of retanning, fatliquoring and dyeing makes matters trickier due to the wide chemical range of the products applied and the very complex variety of mixtures in the discharged floats.

Rules and regulations with respect to the treated effluent discharged have been based on its outflow into the environment. The quality of the water that enters an ETP is of concern to the operators and not to the authorities.

Newer regulations state that „the volume of sewage and contaminant load is to be kept as low as possible by the following measures: …“. In the case of wet-end processing it is required to „reduce the contaminant load in the raw wastewater in wet-end process by the optimizing retanning, dyeing and fatliquoring” (ATV-DVWK-M774 – proposal 2015).

Whereas in the past it sufficed to demonstrate that the outflow from an ETP met with the specific rules and regulations of the local authorities, future requirements will include the need to demonstrate that active efforts have been taken to reduce the inflow’s pollution burden prior to treatment.

The treatment of the discharged float cannot be seen separately from the process it stems from. Processing and effluent water may be identical but are in practice two different departments with little knowledge of each other and unequal levels of attention for their content. The operator of an ETP needs to treat the sewage received from the factory and may not need to have an in-depth knowledge of the effluent-generating processes, yet he or she needs to know what it is that the factory discharges.

The cost of wet-end chemicals discharged into an ETP is threefold and the user pays

1. a price for the unused products
2. the operating cost for removing the unused products from the effluent
3. a fee for the disposal of the sludge

At the end of the wet-end processes in most cases the measure of exhaustion is the visible inspection of the spent floats and a judgement of their transparency and color. A large variety of products creates a mixture of unknown constitution and consistency which can lead to fluctuations and failures in treatment and water quality. Knowing the quantities and of residual chemicals in waste water and their influence on water treatment allows easier and more economical operation of an ETP.

The results discussed in this paper are the outcome of a comparative investigation into fatliquors’ affinity to both chrome (wet blue) and chrome free (wet white) tanned leathers with the purpose of finding tendencies and classifications to predict and control ETP-inflow and treatment.

Based on the percentage exhaustion of individual fatliquors the fatliquors can be allocated in groups for their affinity for leathers of different tannage.

Moreover, the paper makes the assumption that for understanding the effluent load of any tannery wet process the percentage exhaustion does not express the environmental burden of the non-exhausted residue of the process. For a meaningful rendition of the facts the percentage exhaustion is to be replaced by the percentage non-exhausted residue as concentration or oxygen demand of the chemical or its constituents used.

2. MATERIAL AND METHODS

2.1 Materials

In this study chrome–tanned bovine of 1.1–1.2 mm and GTD-pretanned of 1.1–1.2 mm bovine hides set up were used. Both leathers had been produced for automotive application and have been processed according to the recipes in Table **1** (wet blue) and Table 2. (wet white).

Two identical series of commercially available automotive range fatliquors were applied for both applications: polymeric & natural softeners (fatliquor 1), blend of sulphated and sulphited vegetable oils (fatliquor 2), lecithin (fatliquor 4), sulphated vegetable oils (fatliquor 11), blend of sulphited vegetable and animal oils with synthetic oil (fatliquors 3, 8, 9, 10,

12), blend of natural oil with phosphated and succinic acid esters (fatliquors 5 & 7), sulphited fish and animal oil (fatliquor 6).

2.2 Methods

The used processes differed in their design and were formulated considering the specific wet-end processing practices for the two different tannages. The %-ages of fatliquor applied differ: 10% applied for wet blue and 14% application for wet white. Both processes represent simplified forms of commonly applied processes

COD, BOD and TDS determinations were performed at external testing institutes according to ISO 6060:1989 (COD), ISO 1899-1:2003 (BOD) and STAS 9187-84 (TDS)

Further analyses carried out were for TSS, TDS and BOD_5.

A fatliquor's possible contribution to TSS only stems from improper emulsification and is therefore related to the handling of the fatliquor and not the product itself.

Both TDS and BOD_5 demonstrated the same patterns as found with the COD measurement. For this reason the focus of this paper is on COD only.

Table 1. Leather processing recipe – wet blue automotive.

Process		**%**	**Product**	**°C**	**Time**	
wash		300	water	35		
		0,2	formic acid (1:10)		15	3,6
drain						
neutralizing		100	water	35		
		2,5	sodium formate			
		0,7	sodium bicarbonate		45	5,5
drain						
wash		300	water	35	10	
drain						
retanning		100	water	35		
		12	Syntan DM 262		60	
	+	1	formic acid (1:10)		5+15	3,8
drain						
wash		300	water	35	10	
drain						
fatliquoring		100	water	50		
		10	FATLIQUOR		45	
	+	1	formic acid (1:10)		5 + 15	3,6
drain			**float sample**			
cold wash		300	water	25	10	

drain		**float sample**			

Table 2. Leather processing recipe – wet white automotive.

Process		%	Product	Temp °C	Drum Time	pH
wash		300	water	30	20	
drain						
neutralizing		70	water	30		
		2	sodium formate		30	4,8
	+	10	Syntan DM 262		30	
	+	10	Syntan S		330	
	+	100	water	50	10	
	+	1,5	formic acid (1:10)		30	
	+	1,5	formic acid (1:10)		90	3,5
drain						
wash		300	water	35	10	
drain						
fatliquoring		100	water	50		
		14	PRODUCT		60	3.4
	+	1	formic acid (1:10)		10+20	
drain			**float sample**			
cold wash		300	water	25	10	
drain			**float sample**			

3. RESULTS AND DISCUSSION

Twelve commercially available fatliquors have been compared under identical conditions and acidified with a fixed amount of formic acid to the range of 3,5-3,7 for wet blue leathers and 3,3-3,5 for wet white leathers. All values have been based on a) the float before processing, b) the exhausted float after acidifying and c) the subsequent washing float.

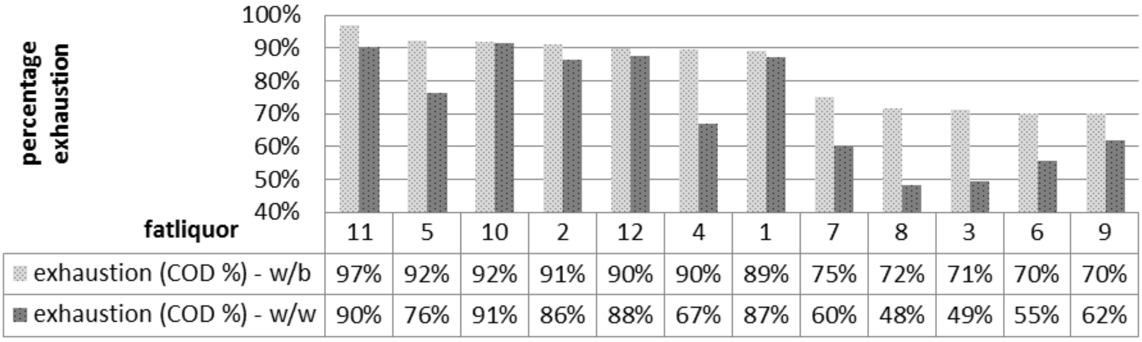
For a first comparison the exhaustion has been expressed in the manner commonly used by the industry as %-age. This %-age relates to the original content of the float minus the residue after processing (original COD – residual COD = exhaustion).

$$\%\ \text{exhaustion} = \frac{\text{amount original float}^{*}}{[\text{amount fixation} + (\text{amount washing x } 3^{**})]}$$

* - 10% for wet blue; 14% for wet white

** - the washing value is multiplied by 3 since the washing float has a length of 300% as compared to 100% float length used for retanning or fatliquoring.

It can be seen from Table 3 that not only between fatliquors the exhaustion %-age greatly varies but that no general relation exists between their use on w/b and w/w.



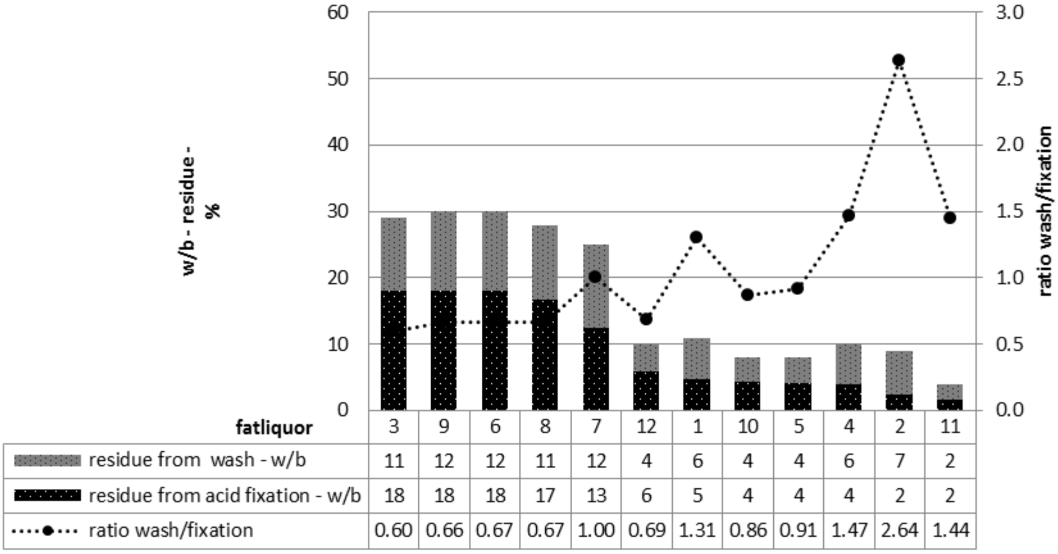
fatliquor	11	5	10	2	12	4	1	7	8	3	6	9
▨ exhaustion (COD %) - w/b	97%	92%	92%	91%	90%	90%	89%	75%	72%	71%	70%	70%
■ exhaustion (COD %) - w/w	90%	76%	91%	86%	88%	67%	87%	60%	48%	49%	55%	62%

Figure 6 exhaustion %-ages of different fatliquors compared for wet blue and wet white processing.

Of the fatliquors with a higher exhaustion %-age (<90%) nrs. 1, 2, 10, 12 demonstrate comparable exhaustion %-ages on both types of tannage, while with nrs. 4 , 5, 11 the w/w exhaustion is inferior to that of w/b .

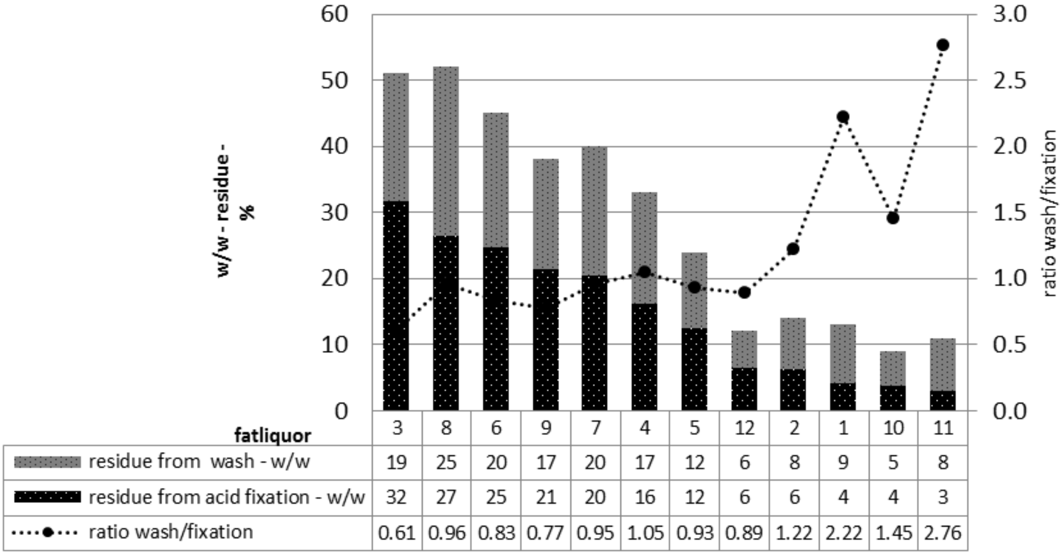
Fatliquors of a lower exhaustion %-age on w/b without exception show inferior exhaustion %-ages to varying degrees when applied on w/w.

Figures 2 & 3 illustrate how much the acidified bath contributes to the total %-age of residue, and how much of the residue has been released by the washing bath.



fatliquor	3	9	6	8	7	12	1	10	5	4	2	11
▨ residue from wash - w/b	11	12	12	11	12	4	6	4	4	6	7	2
■ residue from acid fixation - w/b	18	18	18	17	13	6	5	4	4	4	2	2
···●··· ratio wash/fixation	0.60	0.66	0.67	0.67	1.00	0.69	1.31	0.86	0.91	1.47	2.64	1.44

Figure 2. %-age of generated by different fatliquors on wet blue stemming from the combined acidified and washing floats



fatliquor	3	8	6	9	7	4	5	12	2	1	10	11
▨ residue from wash - w/w	19	25	20	17	20	17	12	6	8	9	5	8
■ residue from acid fixation - w/w	32	27	25	21	20	16	12	6	6	4	4	3
····●···· ratio wash/fixation	0.61	0.96	0.83	0.77	0.95	1.05	0.93	0.89	1.22	2.22	1.45	2.76

Figure 3. %-age of residue generated by different fatliquors on wet blue stemming from the combined acidified and washing floats

Both figures evidence that with increasing amounts of residue in the acidified fatliquor bath the release of unused products by washing increases too.

The ratio between the residues from washing and fixation increases for products that leave only small amounts of residue in the drained float: the bulk of the residue stems from washing. For those fatliquors that leave a large amount of residue it is the other way round: the bulk of their residue stems from acid fixation.

In figures 4 and 5 the %-age of residue is contrasted to the oxygen amount needed for treating the residual float. It can be seen that equal %-ages of exhaustion can represent different degrees of organic pollution. The tables have been prepared from lower to higher exhaustion %-ages to residue make the conclusion more easily visible.

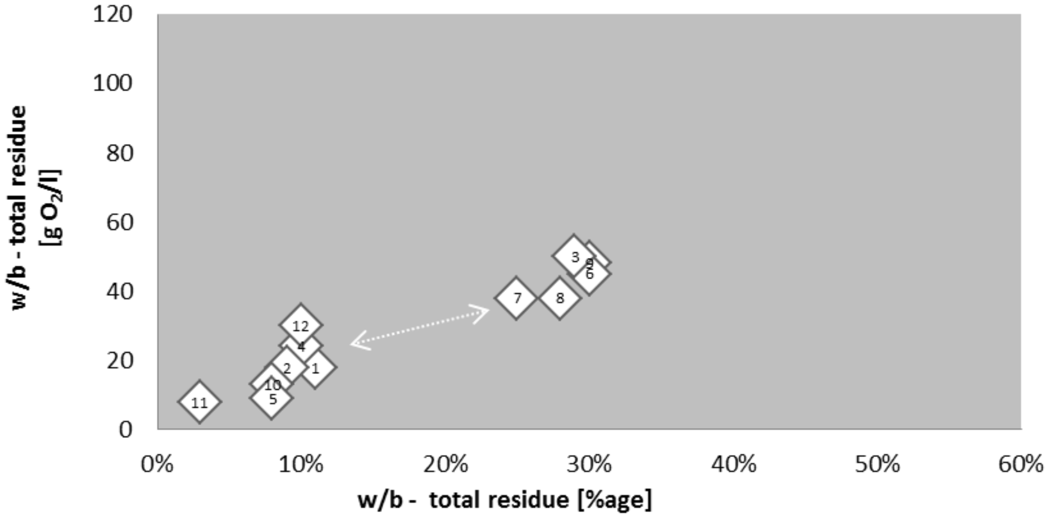


Figure 4. %-age of residue on wet blue in relation to quantity of O_2 required for oxidizing the residual fatliquor

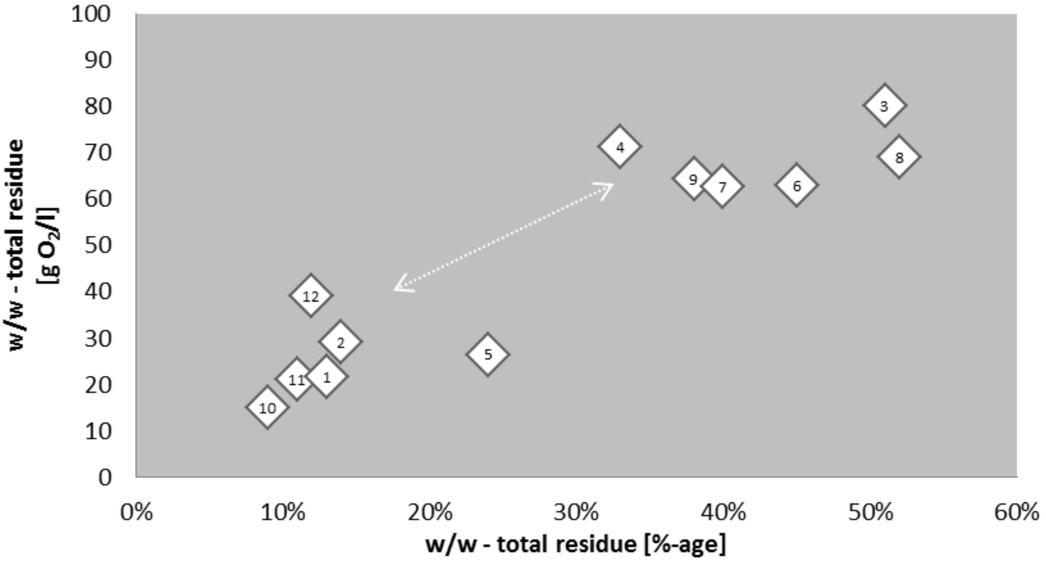


Figure 5. **%-age of residue on wet blue in relation to quantity of O_2 required for oxidizing the residual fatliquor**

In The fatliquors show a particular grouping profile. When used on wet blue, the profiles are notably more specific than when the are applied on wet white.

In both cases a particular gap between the groups is visible.

The exhaustion %-age can also be expressed as a fatliquor's affinity for the substrate it is to react with.

None of the fatliquors shows a better exhaustion rate on wet white than on wet blue. While others show a reduced to significantly reduced tendency for binding to wet white when compared to wet blue.

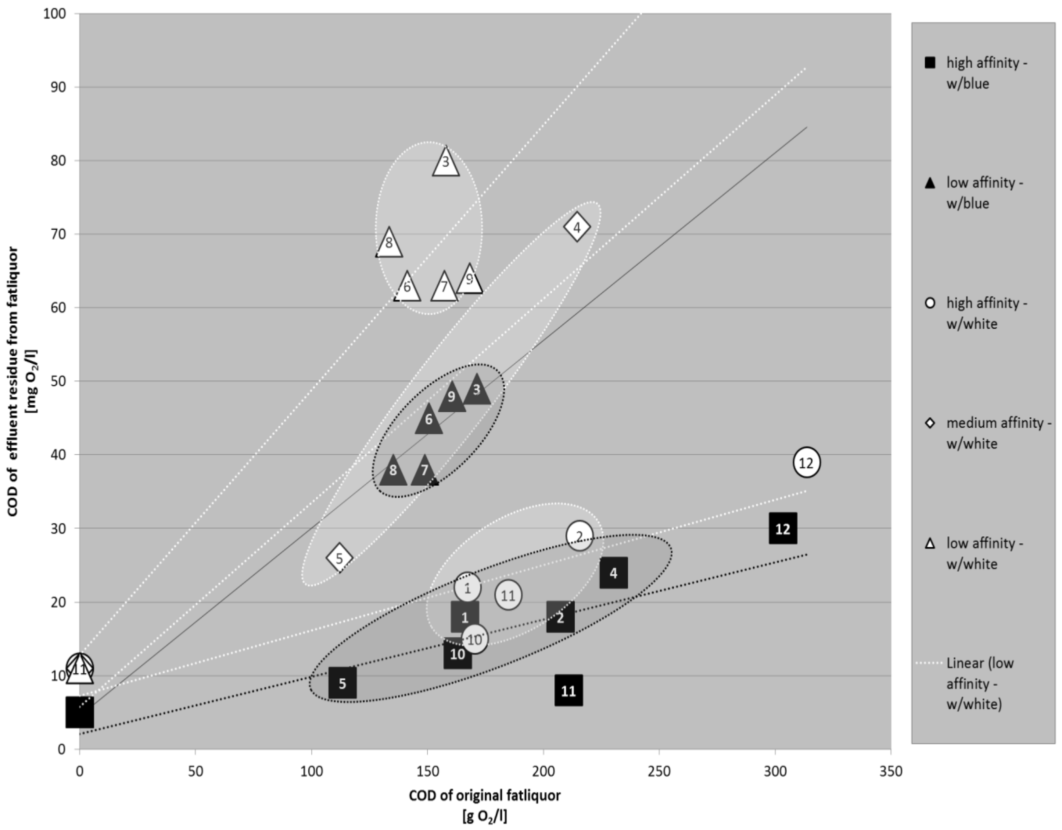


Figure 6. the quantity of O_2 required for oxidizing the unused fatliquor in relation to the quantity of O_2 required for oxidizing the residual fatliquor.

From the effluent data a classification of fatliquors into affinity classes can be made when the individual fatliquor's residual COD is opposed to its initial and unconsumed COD.

The graphic contrasting of the unused fatliquor's initial COD with the COD of the residue it leaves behind does not show a random distribution of properties. Instead it brings to light distinctive groups representing the fatliquors' affinity to the tanned hide.

- Fatliquors of low affinity to both wet blue and wet white are clearly defined groups of comparable initial COD for the products before their use. They are only distinguished by the amount of residue generated by processing wet blue or wet white. The fatliquors of both groups are near- identical.
- Fatliquors of high affinity to wet white are a clearly defined and fairly homogenous group. The height of their residual COD appears to be related to their initial, unconsumed, COD.
- Fatliquors of high affinity to wet blue are less homogeneous in their behavior; their low residual COD value is less related to their initial, unconsumed, COD value.
- Medium affinity is a classification that can only be applied when processing wet white. The group consists of too few fatliquors (2) of a too large band width to clearly identify them. There appears to be a general relation between their initial unconsumed COD value and the residue they generate in the spent floats.
- One fatliquor of high affinity to both wet blue and wet white is separated from all the rest.

4. CONCLUSION & DISCUSSION

Fatliquors to the greatest extent consist of organic compounds. Measuring the float's COD is sufficiently indicative of a fatliquor's degree of exhaustion and the residue it leaves in the drained float.

Based on COD measurements we find patterns that can not be related to the origin and composition of the fatliquors used.

The commonly practiced method to express the exhaustion of fatliquors by the analysis of the exhausted fatliquor float alone overlooks the fact that what is believed to be fixation is to a large degree a reversible binding dependent on pH. The clean float and the pH increase that comes with washing can cause the further release of substantial amount of fatliquors, some of them still unfixed and others previously fixed. For drawing relevant conclusions, washing floats are to be included in any calculation of the kind.

The thus calculated %-age of exhaustion still does not provide any information on the real degree of pollution generated by the residue of a fatliquor. A seemingly good exhaustion can generate considerable pollutant load while, on the other hand a lower exhaustion %-age can be relatively light in pollution burden. The exhaustion expressed as %-age therefore has no value to illustrate a fatliquors quality in environmental terms.

To do so, the oxygen demand needed for converting the residual organic material is a far more suitable criterion to express a fatliquor's environmental impact and compare it to the residues left by other oils.

The tendency to exhaust can be expressed as affinity towards the tanned hide. Of the fatliquors investigated none had a higher affinity for wet white than for wet blue. A small group shows comparable affinity, but most of the oils demonstrate considerably lower affinity.

Randomness appears when attempting to reduce a fatliquor's affinity to its composition or making. None of the affinities found can be attributed to the chemical composition or to any of its main constituents and appears to be a singular property of an individual fatliquor.

The research demonstrated that by applying a simple method and a specific juxtaposition of data yields consistent values to define the affinity of any product towards the tanned hide during processing and the pollution burden after its use. Further research would define whether this behavior depends on a fatliquor's chemical manufacturing and to any of its main constituents, or whether it is independent of this and a is singular property of an individual fatliquor.

6. REFERENCES

Joint Research Centre, Institute for Prospective Technological Studies Sustainable Production and Consumption Unit, European IPPC Bureau, Best Available Techniques (BAT) Reference Document for the Tanning of Hides and Skins, 2013
Feikes L., Ökologische Probleme der Lederindustrie (Bibliothek des Leders) (German Edition), 1983.
Daniels R., Back to Basics: The Environment, 2004.
ATV-DVWK-M774, Abwasser aus lederherstellenden Betrieben, proposal 2015
Ludvic J., The Scope for Decreasing Pollution Load in Leather Processing, 2000.

Buljan J., Kral I., Introduction to Treatment of Tannery Effluents - What every tanner should know about effluent treatment, 2011.
Buljan J., Kral I.,The Framework for Sustainable Leather Manufacture, 2015

IVL O-15

ARTIFICIALLY INDUCED COLLAGEN FIBRIL ORIENTATION AFFECTS TEAR PROPAGATION IN LEATHER

Susyn J. Kelly*, Katie H. Sizeland, Hannah C. Wells, Nigel Kirby, Richard L. Edmonds, Adrian Hawley and Richard G. Haverkamp

School of Engineering and Advanced Technology, Massey University, Private Bag 11222, Palmerston North 4442, New Zealand.
Australian Synchrotron, Blackburn Road, Clayton, Victoria 3168, Australia
Leather and Shoe Research Association, PO Box 8094, Palmerston North 4446, New Zealand.

Ovine leather has around half the strength of bovine leather and is therefore not suitable for high value applications such as shoes. Previously it has been shown that strength in leather correlates with the extent of collagen fibril alignment (orientation index). Here we applied biaxial stretching to ovine skins during tanning. The skins were strained by 10% in two orthogonal directions during the tanning process. Tear strengths were measured by standard methods in two orthogonal directions. Collagen fibril orientation was measured using synchrotron based small angle X-ray scattering. The in-plane collagen fibril orientation index of the manipulated samples rose from 0.4 to 0.6 (p-value = 0.01) (where 0 represents isotropic fibril arrangement and 1 is perfectly parallel fibrils). Biaxial stretching during tanning therefore artificially induces greater collagen orientation. Tear strength increased as orientation index increased from 33 N/mm to 43 N/mm (p-value= 0.03) suggesting that the increase in collagen orientation due to stretching while tanning results in leather of greater strength.

Keywords: collagen, leather, tear strength, small angle x-ray scattering, bi-axial stretching.

INTRODUCTION

Collagen structures provide strength and flexibility in the skin allowing the body to endure stresses and strains. It is the collagen networks in the extracellular matrix that support the cells in the epidermis through structures that strengthen and dissipate forces (Fratzl 2008). Collagen is the most abundant protein in the body with its fibrous nature allowing it to possess a variety of strong and flexible mechanical properties making it suitable to a variety of functions. The function of the collagen is influenced by the load bearing forces on the particular piece of tissue as it is these forces that determine the collagen fibers orientation. Tendons provide a good example of fiber arrangements in response to force. Tough fibrous connective tissues link muscle to bone where the collagen fibers are arranged parallel to load bearing forces giving this tissue the ability to transmit forces and withstand tension during muscle contraction (Franchi et al. 2007). Sophisticated collagen matrixes are present in skin where a more uniform fibril diameter (Ottani et al. 2001) and specific web-like fiber arrangements (Gathercole et al. 1987) influence the tissues strength and location specific behavior. The collagen's ability to rearrange in skin has been primarily attributed to skin's tear resistance, where fibers re-orient to oppose the propagating tear forces (Yang et al. 2015). However, if a tear does manage to propagate the skin heals over this area with scar tissue where again we see the effects of collagen fiber orientations producing certain characteristics. The scar tissue skin which reforms over a wound has collagen fibers with a more parallel alignment (van Zuijlen et al. 2003), a collagen arrangement which has been shown to produce a greater strength (Basil-Jones et al. 2011). When the fibers align in the direction of the straining forces this places the collagen's characteristic triple helix in an optimal position to transpose the forces along its structure (Brodsky & Persikov 2005), increasing the strength of the skin. Normal skin which covers mobile areas like joints have fibers arranged in a more isotropic manner creating a mesh like structure which allows for more flexibility (van Zuijlen et al. 2003).

Collagen structures produce properties in collagen based materials resulting from the fiber arrangement in response to external forces and chemical treatments. Methods to create and manipulate these collagen structures have been of interest for medical tissue engineering applications (Charulatha & Rajaram 2003, Franchi et al. 2007, Freeman & Silver 2005, Gathercole et al. 1987, Kayed et al. 2015, Purslow et al. 1998, Speer et al. 1980, Sturrock et al. 2004) as well as industrial processes like the production of leathers (Basil-Jones et al. 2010b, Basil-Jones et al. 2011, Basil-Jones et al. 2012, Kronick & Buechler 1986, Osaki 1999, Sizeland et al. 2013). Collagen structures can be chemically or mechanically manipulated and these will be considered respectively below. Chemical manipulations target the intra-molecular bonds which form between the fibrils; these are called cross-linkages and are important to the collagen's fibrous structure (Charulatha & Rajaram 2003, Kayed et al. 2015, Zimmermann et al. 1970). Chemical treatments have been investigated to encourage cross-linkages in collagen to increase tissue strength; the most successful of these being treatment with glutaraldehydes to control the properties of the collagen structure (Speer et al. 1980). Leathers tanned with glutaraldehyde have been shown to possess a greater resistance to heat and moisture (Bowes & Cater 1965). While treating the strong collagen based membrane which covers the heart , the pericardium, with glutaraldehye effected the cross-linkages and also the alignment of the collagen fibers (Kayed et al. 2015). Tanning is a sequence of chemical treatments which work to remove non-collagenous material from skins while maintaining the natural collagen structure. The main chemicals used include chromium (III) salts and tannins which increase the denaturation temperature of the leather when compared to skin. This increase in heat resistance is due to cross-linkages formed between the collagen's fibers (Covington et al. 2001).

Applying mechanical strains to collagen based materials has also shown potential to influence the organization of the collagenous matrix by encouraging the fibers to aligning parallel to the straining forces. Leathers have been dried under biaxial stretching forces resulting in an increased tensile modulus and stiffness due to re-orientation of collagen fibers (Sturrock et al. 2004). Not only does this mechanical method influence the collagen matrix applying mechanical strain has also been shown to effect the mineralization of the matrix by altering the locations of the calcium phosphate nucleation sites, important for bone density (Nudelman et al. 2010).

To observe the effects of both chemical and mechanical action on the collagen fibers X-ray scattering has been used to provide insights into collagen fibril orientations and fibril D-spacing (Basil-Jones et al. 2010b, Basil-Jones et al. 2011, Hulmes et al. 1995, Purslow et al. 1998). The technique has also been used to measure the change in collagen fibril alignment in leather under tensile strain (Basil-Jones et al. 2012) where it was shown that fibrils become more oriented up to a certain point after which the collagens ability to re-orient begins to diminish and the forces begin to be observed at an individual fibril level with an increase in d-spacing (Gathercole et al. 1987).

Collagen orientation, which is a measure of fibril alignment relative to one another at a certain azimuthal angle where 1 represents perfect alignment and 0 represents random alignment. The collagen orientation has been investigated in leather and has been shown to have a significant effect on the leathers strength. Collagen fiber alignment appears to have a directly proportional relationship with the strength; where more aligned collagen produces stronger leather with a great variability between various mammals (Sizeland et al. 2013). Ovine leathers are inferior to bovine leathers for high value applications such as footwear due to considerably lower strength resulting from less fibril alignment (Basil-Jones et al. 2011, Basil-Jones et al. 2013). Methods to enhance the strength of ovine leathers could have wide application in the tanning industry to make this leather competitive with those from bovine origins.

Measures of strength have been defined by industry standards in the form of conventional tear test (ISO 3377-2:2002) where the force to tear a sample is measured and used to quantify its strength. Our understanding of skins ability to re-arrange collagen fibers in response to forces to increase strength and resist tear propagation and the effects of tanning on collagen orientation suggests two mechanisms which could provide the potential to enhance leather strength.

Here we performed structural and mechanical studies to determine firstly if mechanical collagen realignment while tanning in skin was possible and if the realignment would be permanent after tanning and secondly we examined the effects of this realignment on the strength, or resistance to tear propagation, of the leather produced.

MATERIAL AND METHODS

Leather was prepared from ovine pelts using conventional beamhouse and tanning processes. The ovine pelts were from 8 to 10 month old New Zealand Romney sheep from the wider Manawatu region**.** After rehydrating the skins, adhering fat and flesh was removed mechanically and conventional lime sulphide paint (140 g/L sodium sulphide, 50 g/L hydrated lime and 23 g/L pregelled starch thickener) was applied to the flesh side of the skin at a rate of 400g/m^2. Following incubation at 20 °C for 16 hours keratinaceous materials were removed and the skins washed in water to remove the lime. Following the last wash ammonium sulphite was added into the water to lower the pH to 8 and a commercial bate enzyme, Tanzyme (0.1% (w/v)), was added before the skins were incubated at 35 °C for 75 min. Following further washing in water the skins were pickled in 20% (w/v) sodium chloride and 2% (w/v) sulphuric acid.

Control and test leather samples (each 270 x 270 mm) were obtained from the pelts at the official sampling positions with the orientation to the backbone recorded for all samples. See **Figure 1** for details. The test squares were mounted in a custom made biaxial stretching device which applied and maintained stretch during the beamhouse and tanning process. Samples were processed with even bi-axial forces applying a stretch force lengthened the samples by 10% in both directions. The control samples were processed without tension.

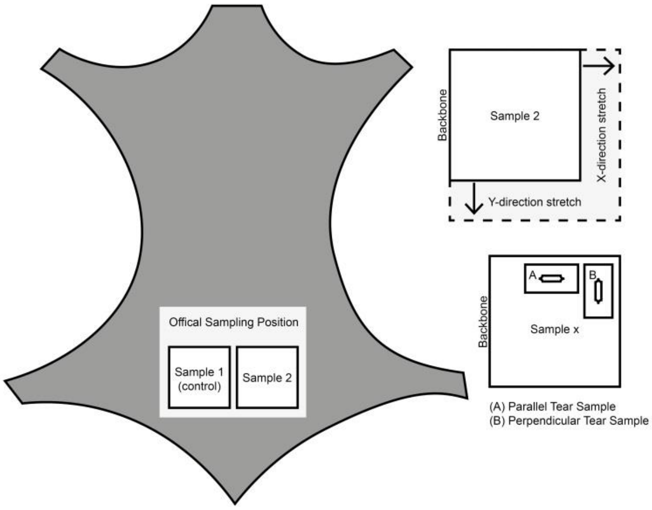


Figure 1: Sampling positions for stretching and tearing from the official sample position (OSP) on the Ovine skin.

Following pickling the control and test samples were degreased in 4% non-ionic surfactant (Tetrapol LTN, Shamrock, New Zealand) for 90 min and then washed. After being neutralized in a 1% disodium phthalate solution (Feliderm DP, Clariant, U.K) for 30 min. the samples were process overnight at 25 °C in a 5% chrome sulphate solution (Chromosal B, Lanxess, Germany). The following day the samples were neutralized in 1% sodium formate and 0.15% sodium bicarbonate solution for 1 hour, washed in water, and retanned with 2% synthetic retanning agent (Tanicor PW, Clariant, Germany) and 3% vegetable tanning (mimosa) (Tanac, Montenegro, Brazil). Finally the skins were treated with a 6% fatliquor solution and fixed with 0.5% formic acid for 30 min. After a final wash in cold water the stretched samples were removed from the biaxial stretching devices and left to dry with the control samples.

Tear strengths were measured according to standard methods (ref ISO 3377-2:2002) and normalized for thickness. Samples were cut from the official sampling position and treated at constant environment conditions (20 °C and 65% relative humidity) for 24 hours before tear strengths were recorded on an Instron 4467 instrument.

For SAXS analysis squares (5 x 5 mm) we taken to perform edge-on measurements were analysis was performed vertically across a cross section of the sample from the grain surface to the corium of the leather. These were mounted normal to the X-ray beam without tension. Six measurements were recorded spanning the cross section with a 0.1 mm sample spacing between points.

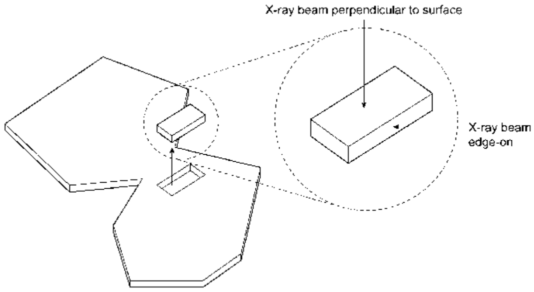


Figure 2: Orientation of sample relative to the X-ray beam to produce edge-on measurements.

The diffraction patterns were recorded on the Australian Synchrotron SAXS/WAXS beamline. A high-intensity undulator source was utilized with an energy resolution of 10^{-4} from a cryo-cooled Si(111) double-crystal monochromator. The beam size (fwhm focused at the sample) was 250 x 80 µm with a total photon flux of about 2 x 10^{12} photons s^{-1}. All diffraction patterns were recorded with an X-ray energy of 8 keV using a Pilatus 1M detector with an active area of 170 x 170 mm and a sample to detector distance of 3371 mm. The exposure time for diffraction patterns was in the range of 1- 5 seconds, and data processing was carried out using the SAXS15ID software (Cookson et al. 2006). Intensities displayed are all absolute detector counts (one X-ray detected one detector count), except where stated otherwise.

The collagen orientation was determined from the azimuthal angle for the maximum intensity of the D-spacing diffraction peaks. The orientation index (OI) was the primary measure used where OI is defined as (90 °−OA)/90 °, where OA is the minimal azimuthal angle range, centred at 180 °, that contains 50% of the micro fibrils (Basil-Jones et al. 2010a, Sacks et al. 1997). The OI range takes us from perfect alignment which is represented by an OI of 1, through to an OI of 0 which suggests high miss aliment or isotropy. The OI was calculated from the spread in the azimuthal angle of the D-spacing peak at 0.059 − 0.060 $Å^{-1}$. Each OI value presented here represents the average of 14 − 36 measurements of one sample.

RESULTS AND DISCUSSION

Sample sets were cut from different animal skins and were composed of a stretched sample and its non-stretched counterpart. These samples had a series of tear tests performed at two orientations, perpendicular and parallel, relative to the backbone with their normalized tear strengths calculated to show the effects of stretching, Table 1. To contribute to understanding the variation in tear strength due to the effects of stretching orientation index measurements (OI) we determined through SAXS imaging.

Sample	x direction stretch (% of length gained)	y direction stretch (% of length gained)	Normalized Tear Force (parallel) (N/mm)	Normalized Tear Force (perpendicular) (N/mm)	OI (edge on)
1	10	10	38.0	46.2	0.5
1 (c)	0	0	36.6	42.6	0.5
2	10	10	38.8	41.4	0.7
2 (c)	0	0	25.6	27.0	0.4
3	10	10	36.9	41.0	0.7
3 (c)	0	0	25.5	28.8	0.5

Table 1: Sample matrix showing the tear strength, normalized for thickness, in both parallel and perpendicular directions relative to the animals backbone and the edge-on orientation index (OI).

The SAXS patterns of the samples placed under biaxial stretching can be compared with those processed normally revelled a change in the orientation of the collagen fibres. The scatter patterns (**Figure 2**, left) show the fibres angular distribution to be more uniformly oriented in the stretched sample (**Figure 2**, top) with greater peak intensities laying along the plane of the stretch forces (0° and 180°, where 90° represents alignment from the grain to corium). The sample tanned without strain on the other hand has a more circular intensity pattern suggesting a more isotropic arrangement where fibres are more randomly arranged between the grain and corium.

Plots of a single meridional arc at q~0.05 Å^{-1} (right) again shows the stretched sample as having a greater preferred fibre orientation with greater intensity peaks at 0 ° and 180 °. The un-stretched sample has lower intensity peaks and a more narrow spread of fibres oriented around the preferred direction.

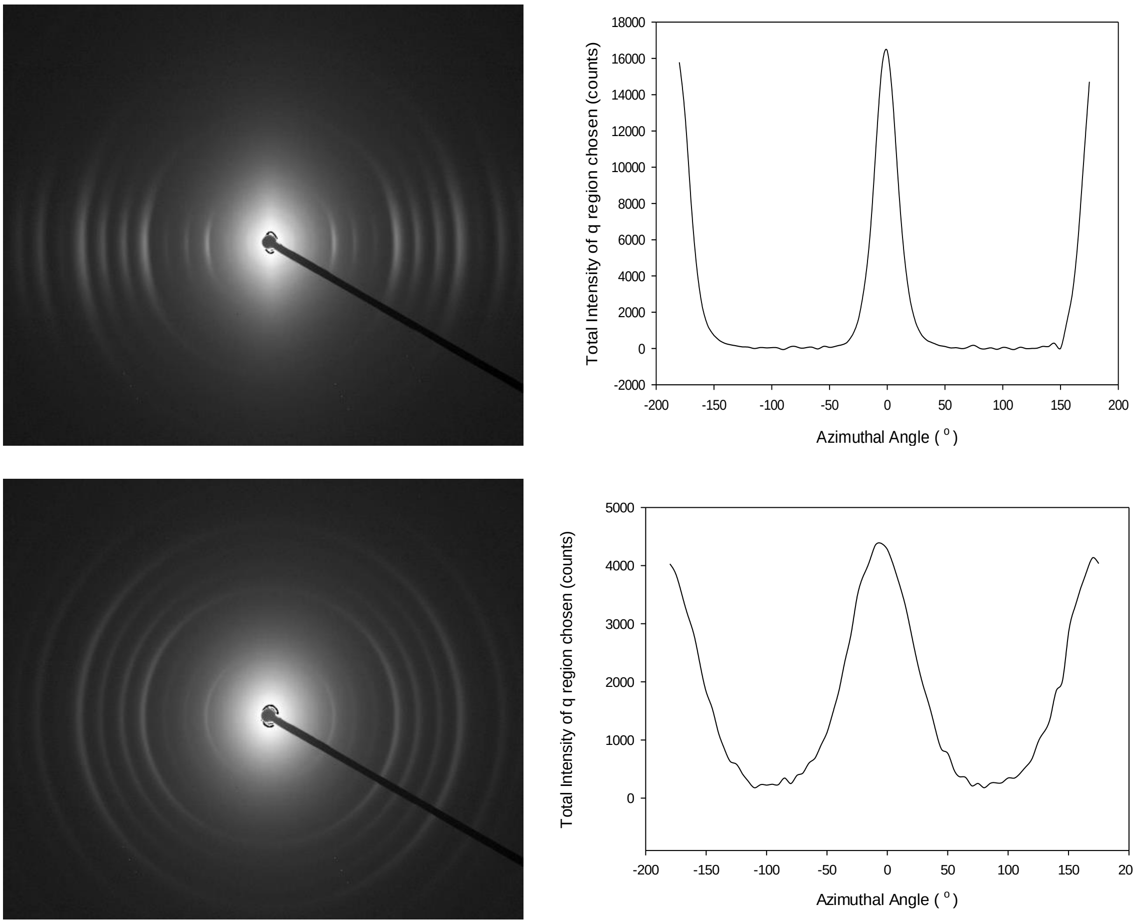


Figure 2: Example of SAXS scatter patterns (left) and their corresponding integrated intensity plots around the 5th diffraction peak (I versus q) for edge-on imaging of a stretched leather sample (top) and a normal, non-stretched, leather sample (bottom).

Applying bi-axial stretching forces in the X and Y directions produces a statistically significant change in collagen orientation (edge-on OI of 0.43 (non-stretched sample) versus 0.64 (Stretched sample), p-value = 0.01) (**Figure 3**). In applying bi-axial stretching forces to skins before tanning we increase the orientation index (OI). A change in the OI, when compared with the normal, non-stretched samples, demonstrates collagen re-alignment has occurred where fibers have been encouraged to become more oriented in the direction of the stretch forces. This produces leather with more anisotropic characteristics where fibers are more like a laminate and lie in the plane of the leather as suggested by **Figure 2**.

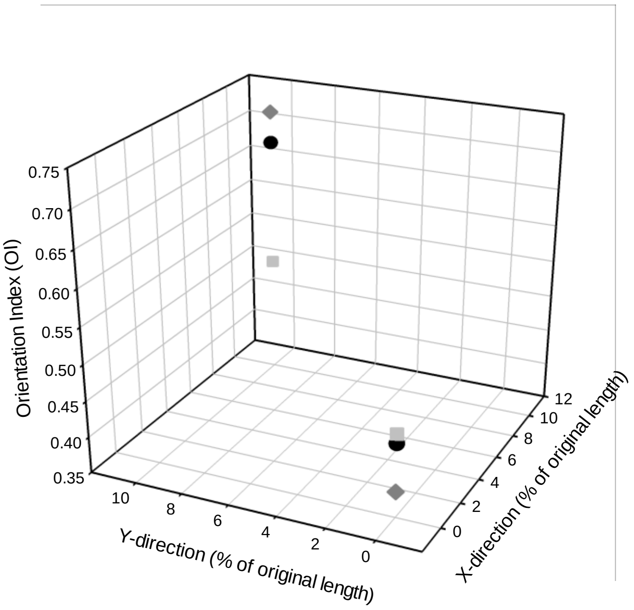


Figure 3: 3D plot of y-direction stretch and the x-direction stretch applied to the sample corresponding in to the edge-on orientation index (OI). The different colors represent different sample replicates.

The double edge tear test has been used as a measure of leather strength (ISO 3377-1:2011). The standard requires two types of tear samples to be taken. What differentiates these two types of samples is their orientation to the backbone; one is taken parallel and the other perpendicular (**Figure 1**). The reason for taking samples in two directions is due to the natural collagen alignment observed in skins which are arranged for functional purposes while on the animal (Osaki 1999). This region is defined as the official sampling position (OSP) providing the best location to sample skins (ISO/FDIS 2418). The standard requires tear samples be taken from here. The natural alignment found in skins results in the perpendicular tear strength measure tending to require a greater tear force than that is required when tearing is propagated parallel to these fibers. We observe this here when comparing the two tear tests in **Figure 4** (parallel tear force (left); perpendicular tear force (right)).We can also see that the stretched samples have a greater overall tear strength in both sample tear directions (parallel, 29N/mm versus 38N/mm, p-value = 0.02 and perpendicular, 33 N/mm versus 43 N/mm p-value = 0.03 to the backbone).

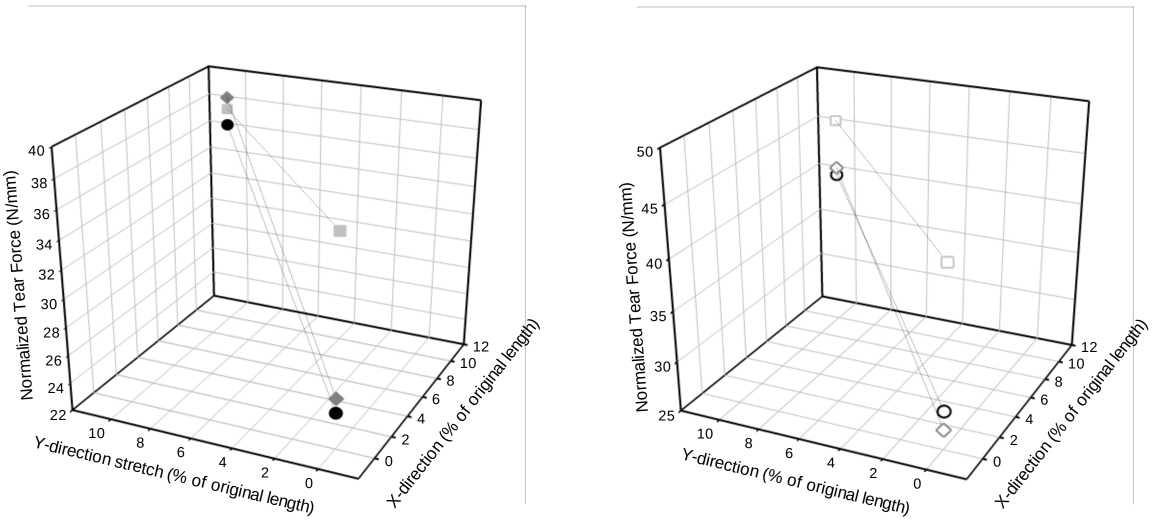


Figure 4: 3D plot of y-direction stretch and the x-direction stretch applied to the sample corresponding in to the parallel (filled shapes, left) and perpendicular (shape outlines, right) tear strength positions relative to the backbone, normalized for thickness in N/mm. The different colors represent different sample replicates.

Corium thickness has been attributed to strength and it is worth noting that this thickness has not been considered here. A thicker corium layer would contribute significantly to strength as it contains a greater concentration of collagen which is more highly oriented and has a shorter d-spacing (Oleary & Attenburrow 1996).

Correlating the collagen fiber orientations with the tear strengths we notice a linear trend where a greater OI results in greater tear strengths, **Figure 5**. This relationship is true for both tear directions and the application of bi-axial straining forces while tanning exaggerates these effects. Stretched samples have greater overall tear strength in both tear directions when compared with their non-stretched counterparts (**Figure 5**).

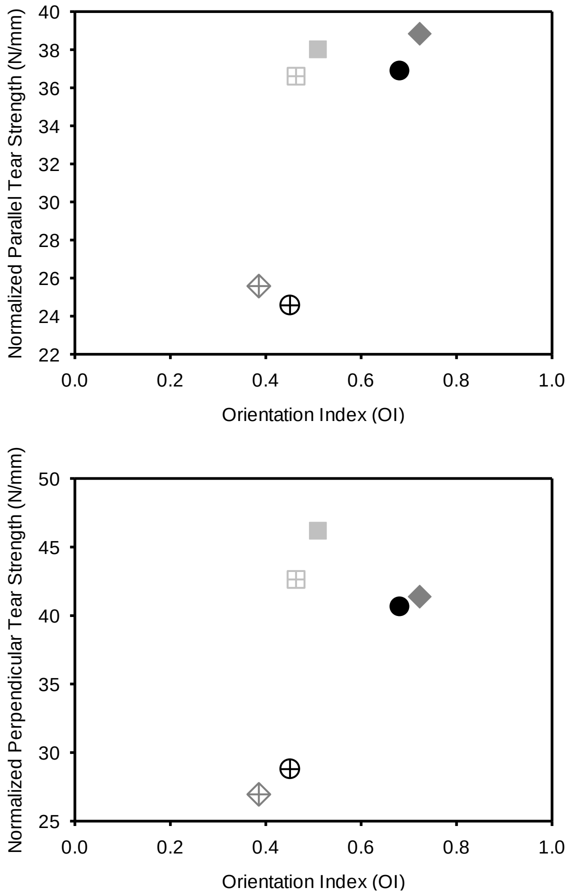


Figure 5: Edge on orientation index (OI) versus normalized tear forces parallel to the backbone (shape outline) and perpendicular to the backbone (filled shapes). The different colors represent different sample replicates where points with cross-hairs are the controlled, non-stretched samples.

CONCLUSION

Preliminary results show that applying even bi-axial stretching forces to skins during tanning results in leathers of greater strength. SAXS has shown the collagen fibrils re-orient in the direction of the stretching forces producing an increase in the edge-on OI. These leathers display a greater tear strength which can be correlated to the greater collagen alignment (Basil-Jones et al. 2012, Sizeland et al. 2013).

To better utilize the effects of stretching on collagen alignment in skins, considerations into the natural collagen alignment could allow for better customizations in the application of stretching forces to produce specific results in the leathers produced. By applying uneven stretch forces can we enhance natural alignment? Or if we apply greater straining forces perpendicular to the natural alignment can we reform the collagen arrangement to something more customized and suited to the end product?

ACKNOWLEDGEMENTS

This research was undertaken on the SAXS/WAXS beamline at the Australian Synchrotron, Victoria Australian. Nigel Kirby, Tim Ryan, Adrian Hawley and Stephen Mudie assisted with data collection and processing. Richard Edmonds and Geoff Holmes from New Zealand Leather and Shoe Research (LASRA) assisted with experimental design and data collection.

REFERENCES

1. Basil-Jones MM, Edmonds RL, Allsop TF, Cooper SM, Holmes G, Norris GE, Cookson DJ, Kirby N & Haverkamp RG (2010a): Leather structure determination by small-angle X-ray scattering (SAXS): Cross sections of ovine and bovine leather. J. Agric. Food Chem. **58**, 5286-5291.
2. Basil-Jones MM, Edmonds RL, Allsop TF, Cooper SM, Holmes G, Norris GE, Cookson DJ, Kirby N & Haverkamp RG (2010b): Leather structure determination by small angle X-ray scattering (SAXS): Cross sections of ovine and bovine leather. J. Agric. Food Chem. **58**, 5286-5291.
3. Basil-Jones MM, Edmonds RL, Cooper SM & Haverkamp RG (2011): Collagen fibril orientation in ovine and bovine leather affects strength: A small angle X-ray scattering (SAXS) study. J. Agric. Food Chem. **59**, 9972-9979.
4. Basil-Jones MM, Edmonds RL, Cooper SM, Kirby N, Hawley A & Haverkamp RG (2013): Collagen Fibril Orientation and Tear Strength across Ovine Skins. Journal of Agricultural and Food Chemistry **61**, 12327-12332.
5. Basil-Jones MM, Edmonds RL, Norris GE & Haverkamp RG (2012): Collagen fibril alignment and deformation during tensile strain of leather: A small-angle X-ray scattering study. J. Agric. Food Chem. **60**, 1201-1208.
6. Bowes JH & Cater CW (1965): Crosslinking of collagen. Journal of Applied Chemistry **15**, 296-304.
7. Brodsky B & Persikov AV (2005) Molecular Structure of the Collagen Triple Helix. In Advances in Protein Chemistry. Academic Press, pp. 301-339.
8. Charulatha V & Rajaram A (2003): Influence of different crosslinking treatments on the physical properties of collagen membranes. Biomaterials **24**, 759-767.
9. Cookson D, Kirby N, Knott R, Lee M & Schultz D (2006): Strategies for data collection and calibration with a pinhole-geometry SAXS instrument on a synchrotron beamline. J. Synchrotron Radiat. **13**, 440-444.
10. Covington AD, Lampard GS, Menders O, Chadwick AV, Rafeletos G & O'Brien P (2001): Extanded X-ray absorption fine structure sudies of the role of chromium in leather tanning. Polyhedron **20**, 461-466.
11. Franchi M, Trirè A, Quaranta M, Orsini E & Ottani V (2007): Collagen Structure of Tendon Relates to Function. Thescientificworldjournal **7**.

12. Fratzl P (2008) Collagen: Structure and Mechanics, an Introduction. In Collagen: Structure and Mechanics (Fratzl P ed.). Springer US, Boston, MA, pp. 1-13.
13. Freeman JW & Silver FH (2005): The effects of prestrain and collagen fibril alignment on in vitro mineralization of self-assembled collagen fibers. Connect Tissue Res **46**, 107-115.
14. Gathercole LJ, Shah JS & Nave C (1987): Skin-tendon differences in collagen D-period are not geometric or stretch-related artefacts. International Journal of Biological Macromolecules **9**, 181-183.
15. Hulmes DJ, Wess TJ, Prockop DJ & Fratzl P (1995): Radial packing, order, and disorder in collagen fibrils. Biophysical Journal **68**, 1661-1670.
16. Kayed HR, Sizeland KH, Kirby N, Hawley A, Mudie ST & Haverkamp RG (2015): Collagen Cross Linking and Fibril Alignment in Pericardium. RSC Adv. **5**, 3611-3618
17. Kronick PL & Buechler PR (1986): Fiber orientation in calfskin by laser-light scattering or X-ray-diffraction and quantitative relation to mechanical-properties. J. Am. Leather Chem. Assoc. **81**, 221-230.
18. Nudelman F, Pieterse K, George A, Bomans PHH, Friedrich H, Brylka LJ, Hilbers PAJ, de With G & Sommerdijk NAJM (2010): The role of collagen in bone apatite formation in the presence of hydroxyapatite nucleation inhibitors. Nat Mater **9**, 1004-1009.
19. O'leary DN & Attenburrow GE (1996): Differences in strength between the grain and corium layers of leather. Journal of Materials Science **31**, 5677-5682.
20. Osaki S (1999): Distribution map of collagen fiber orientation in a whole calf skin. Anat. Rec. **254**, 147-152.
21. Ottani V, Raspanti M & Ruggeri A (2001): Collagen structure and functional implications. Micron **32**, 252-260.
22. Purslow PP, Wess TJ & Hukins DW (1998): Collagen orientation and molecular spacing during creep and stress-relaxation in soft connective tissues. The Journal of Experimental Biology **201**, 135-142.
23. Sacks MS, Smith DB & Hiester ED (1997): A small angle light scattering device for planar connective tissue microstructural analysis. Ann. Biomed. Eng. **25**, 678-689.
24. Sizeland KH, Basil-Jones MM, Edmonds RL, Cooper SM, Kirby N, Hawley A & Haverkamp RG (2013): Collagen Orientation and Leather Strength for Selected Mammals. Journal of Agricultural and Food Chemistry **61**, 887-892.
25. Speer DP, Chvapil M, Eskelson CD & Ulreich J (1980): Biological effects of residual glutaraldehyde in glutaraldehyde-tanned collagen biomaterials. Journal of Biomedical Materials Research **14**, 753-764.
26. Sturrock EJ, Boote C, Attenburrow GE & Meek KM (2004): The effects of the biaxial stretching of leather on fibre orientation and tensile modulus. Journal of Materials Science **39**, 2481-2486.
27. van Zuijlen PPM, Ruurda JJB, van Veen HA, van Marle J, van Trier AJM, Groenevelt F, Kreis RW & Middelkoop E (2003): Collagen morphology in human skin and scar tissue: no adaptations in response to mechanical loading at joints. Burns **29**, 423-431.
28. Yang W, Sherman VR, Gludovatz B, Schaible E, Stewart P, Ritchie RO & Meyers MA (2015): On the tear resistance of skin. Nature Communications **6**.
29. Zimmermann BK, Pikkarainen J, Fietzek PP & Kühn K (1970): Cross-Linkages in Collagen. European Journal of Biochemistry **16**, 217-225.

IVL O-16

CHROME-FREE TANNAGE: SUEDE GARMENT LEATHERS FROM RURAL VEGETABLE SHEEP CRUST LEATHERS

A.E Musa* and G.A Gasmelseed

Department of Leather Technology, College of Applied and Industrial Sciences, University of Bahri,
Khartoum, Sudan, P.O.Box 12327
E mail: musaalileather@gmail.com

Department of Chemical Engineering, Faculty of Engineering, University of Science and Technology,
Khartoum, Sudan
E mail: gurashigar@hotmail.com

Worldwide research is being focused on chrome-free tanning systems. Many studies based on less chrome and chrome-less technologies have emerged in the recent past. The tannin molecules in vegetable tanned leathers form multiple hydrogen bonds with collagen and create a polyphenolic tanning matrix. The hydrothermal stability of vegetable tanned leather is in the range of 70-85°C. By retanning of vegetable tanned leather with metals the shrinkage temperature (Ts) can be elevated considerably in a process that is commonly known as semi-metal tanning. Semi-metal tanning systems have gained importance in recent times as an alternative for chrome tanning. In this study, an attempt has been made to manufacture of semi-alum garment leathers from sheep rural garad tanned crust leathers. Sheep rural garad tanned crust leathers carefully sorted for size, substance, and grain quality, so that the customers' requirements can be met accurately. The selected crust leathers followed the subsequent processing, viz, stripping, bleaching, retannage with aluminium sulphate prepared solution, neutralization, dyeing, fatliquoring, drying and finishing. Full chrome tanned garment leathers from sheep skins used as control leathers. The physical and chemical characteristics of experimental leathers are comparable to control leathers. The experimental trial resulted in very soft and flexible leathers with high tensile strength. However, the stripped rural garad tanned leather retanned with 2% Al_2O_3; resulted in shrinkage temperature of 102°C. The experimental trial resulted in leathers with good organoleptic and strength properties. The semi-alum tanning system provides significant reduction in the discharge of total dissolved solids in the wastewater. The work presented in this paper established the use of semi-alum tanning system as an effective alternative cleaner tanning methodology

Keywords: Garad, Semi-alum, Stripping, Shrinkage temperature, Crust leather

INTRODUCTION

The skins of all animals have, in their time, been used for garments. However, because this is the most worthwhile use for them, most clothing leathers are now made from the skins of woolled sheep or lambs killed for the meat trade. Other sheepskins, such as those of hair sheep, tanned primarily for glove leather, are also used for clothing. Much clothing leather is made from East Indian and other vegetable tanned sheep and goat skins after a chrome retannage. Both grain and flesh splits from bovines are also used. The latter often provide a particularly inexpensive raw material, but in all these cases the original tannage is not specifically designed for clothing leathers.[1]

The substance of garment leather must be uniform and varies between 0.5- 0.8 mm (suede garment) or between 0.6-0.8 mm (grain garment). The substances of lower grades are sometimes kept between 0.8-1.0 mm. The garment leathers must be of light weight, soft and flexible with some amount of 'spring' but should never be too stretchy to make the garment de-shaped during wear. The other desirable properties of clothing leathers are a good drape, uniform appearance, low density and a satisfactory tear-strength.

Leather tanning is dominated by the use of chromium (III) salts, because it gives leather unmatchable hydrothermal stability and excellent organoleptic properties. However, chrome tanning has some negative attributes, posing serious challenges to our continued reliance on it. As a limited resource, chromium (VI) is a well-known carcinogen, but chromium(III) is considered as non-toxic. The chromium (III) existing in leather might be transformed into chromium(VI) in some extreme conditions. Therefore, the chrome remaining in wastewater and the solid wastes may be harmful to the environment. Nevertheless, the one property, which chromium has not been able to provide is fullness, as chrome tanning alone is known to produce leathers which are empty in nature.

Vegetable tanning has been considered as a suitable ecofriendly option to replace chromium. However, vegetable tanning has some shortcomings such as the fullness of vegetable leathers which prevents its use for some end products. Vegetable tannins are also difficult to biodegrade. Amongst mineral tanning agents, aluminium, titanium, iron, zirconium have been explored for their solo tanning potential but each one has associated disadvantages. Iron tanned leathers darken during ageing, zirconium salts are high cost items and the hydrothermal stability of aluminium tanned leathers is low compared to chrome tanned. Combination tannages are thus being considered as suitable alternatives for chrome-free tanning systems.

In vegetable tanned leathers, tannin molecules form multiple hydrogen bonds with collagen and create a polyphenolic tanning matrix. The shrinkage temperature (Ts) of vegetable tanned leather is in the range of 70-85°C. By retanning with metals such as aluminium the Ts of vegetable tanned leather can be elevated considerably in a process that is commonly known as semi-alum tanning. Similarly, retanning of vegetable tanned leather with metal salts has been referred to as semi-metal tanning.

Semi-chrome leather is used as substitute for chromium tanned goatskin, particularly when a heavier substance is required, for example, for unlined casual footwear and slippers. The classical raw material for this leather is East Indian goatskin from India exported in the lightly vegetable tanned crust state. Alternative and expanding supplies are available from Pakistan, East and West Africa, and the Middle Eastern countries. The quality of these leathers has improved recently as far as the process in itself is concerned; but commercial factors affect their qualities, which suffer from the fact that these skins are mainly produced by small tanners, who cannot afford the high prices paid by the larger chrome tanners for their raw skins. These leathers are sold by weight in the crust, so that they are often adulterated with Epsom salts (magnesium sulphate), colloidal earths, added fats. The incidence of faults attributable to the presence of large quantities of natural and added fats in increasing, particularly in suede leathers, so that solvent degreasing of the crust goatskins is being carried out by some dressers.

Semi-chrome leather is first vegetable tanned and subsequently retanned with chrome salts. The accepted model of the principal interaction in semi-metal tanning is based on complexation of metal ion by the metal-polyphenol (**Fig. I**). The chelated complexation of the metal centre creates crosslinks in the polyphenolic tanning matrix resulting in the formation of an extended supramolecular tanning matrix around the collagen. Subsequently, the shrinkage temperature is increased considerably.

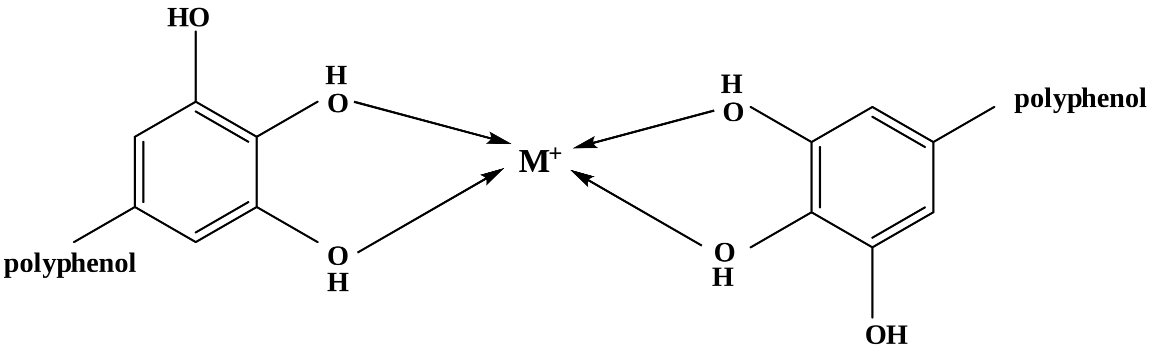


Figure 1: Basis of the semi-metal tanning reaction (Covington, 2009)

Acacia nilotica pods which are widely used by the industry in both the rural and mechanized sectors has been given different names by different tribes viz. Bagaruwa or Gabaruwa (Hausa in Negeria) and Sunt-garad (Sudan)[15] . Sudan has various indigenous tanning materials. Some of these, such as Garad pods (Acacia nilotica sub. sp. nilotica) and Talh bark (Acacia seyal) are used extensively in the Sudan by rural tanners. The tannin content of garad pods is fairly high and amounts to approximately 30% of the total weight, soluble nontans are nearly 20%, while moisture and insolubles make up the remainder. The main constituent of the garad tannin is presumably leucocyanidin gallate i.e. gallic acid esterified with a flavanoid. Garad tannin is reported to contain chebulinic acid, gallic acid and to have a high sugar content, factors which are common in hydrolysable tanning materials. Garad tannins are therefore mixed tannins i.e. containing condensed tannins as well as hydrolysable tannins containing gallic acid esterified with glucose[16]. The basic objective of this study is to develop a chrome free tanning system based on a semi-metal from rural vegetable tanned crust leathers for production of garment leather.

MATERIALS AND METHODS

Materials

Sheep rural garad tanned crust leathers without any grain defects have been taken for tanning trials. The selected leathers dipped in water, piled for several hours to condition uniformity, and then shaved at thickness 0.8 mm. The usual process consists of wetting back , stripping, bleaching, retanning with aluminium salt solution, neutralization, dyeing, fatliquoring, drying, and finishing. The leathers are weight after shaving. The aim of stripping is a light detannage in order to obtain increased uptake of aluminium sulphate salts. Chemicals used for post tanning processes have been of commercial grade. Chemicals used for the analysis of spent liquor have been of analytical reagents.

Basic Aluminum sulphate solution

A known amount of Aluminum sulphate has been taken in a beaker and 150% of water (% based on the weight of Aluminum sulphate) has been added and the solution stirred for 15-20 minutes, subsequently required amount of ligand (sodium citrate and sodium tartrate) have been added and stirring has been continued for 45 min followed by slow addition of sodium carbonate until the pH has been raised to 3.5. For 0.5M of Aluminum sulphate 0.1M of ligand has been added.

Methods

Procedure for processing the garment leathers

The experimental process for rural garad tanned crust leathers is given in Table I. The amount of aluminum sulphate used for the experimental trial is 2% Al_2O_3. The control process for full chrome garment leather from Sheep skins using 8% basic chromium sulphate (BCS), is given in Table II. The post tanning process as mentioned in Table III has been followed for experimental and control leathers.

Shrinkage temperature

The shrinkage temperature of control and experimental leathers has been determined using Theis shrinkage tester[17]. 2X0.5 cm^2 piece of tanned leather cut from the official sampling position has been clamped between the jaws of the clamp and has been immersed in solution containing 3:1 glycerol: water mixture. The solution has been continuously stirred using mechanical stirrer attached to the shrinkage tester. The temperature of the solution has been gradually increased and the temperature at which the sample shrinks has been measured as the shrinkage temperature of the leathers.

Table I

Recipe of the experimental trial for semi-alum leathers from sheep

Rural garad tanned crust leathers

Process	%	Chemicals	Duration (min)	Remarks
Washing	100	water	15	
Stripping	100 1	Water Sodium bicarbonate	60	Single feed, washed well after stripping
Bleaching	100 1	Water Oxalic acid	60	1 feed, pH should be 3.5 drain 50% of bath
Semi alum tanning	2	Al_2O_3 (prepared Aluminium sulphate solution))	90	Check for penetration in cross section
Basification	0.75	Sodium bicarbonate	3× 15	Check the pH to be 4. Drain the bath and pile overnight. Next day sammed and shaved to 0.8 mm. The shaved weight noted.

Table II

Recipe of the control trial for full chrome garment leather from Sheep skins

Process	%	Product	Duration (min)	Remarks
Soaking	200	Water		
Painting	10	Water		
	2	Sodium sulphide		
	4	Lime		Apply the paste on to the flesh side and pile over night. Next day unhairing.
Reliming	100	Water		
	8	Lime		Dip the unhaired skins in this lime liquor for 2 days. Then do fleshing
Deliming and Bating	100	Water		
	1	Ammonium Chloride	60	
	0.25	Bating Agent	60	pH 8-8.5
Pickling	100	Water		
	10	Salt	10	^{o}Be 6-7
	0.2	Formic Acid		
	1	Sulphuric Acid	3x15+45	pH 2.8-3 , Two day ageing
Chrome tanning	50	Pickle float		
	50	water		
	8	Basic Chromium Sulphate	90	
Basification	1	Sodium formate	20	
	1	Sodium bicarbonate	3x15+45	Check the pH to be 4. Drain the bath and pile overnight. Next day sammed and shaved to 0.8 mm. The shaved weight noted.

Physical testing

The leathers were sampled as per IULTCS methods[18] and conditioned at 80±4ºF /65±2 % R.H. for 48 hrs. Tensile strength, elongation, tear strength and grain crack were investigated as per standard procedures. Each value reported is an average of four tests (2 along the backbone, 2 across the backbone).

Organoleptic properties

Experimental and control crust leathers have also been assessed for softness, fullness, grain smoothness, grain tightness (break), general appearance and dye uniformity by hand and visual examination. Three experienced tanners rated the leathers on a scale of 0-10 points for each functional property, where higher values indicate better property of leathers.

Analysis of spent tan liquor

The spent liquor from control and experimental tanning processing were collected, filtered and analyzed for chemical oxygen demand (COD), Biochemical oxygen demand (BOD_5), and total Dissolve solids (TDS) as per standard procedures.

Chemical Analysis

The chemical analysis of the leathers viz. for total ash content, % moisture, % oils and fats, % water soluble, % hide substance, % insoluble ash and degree of tannage were carried out for control and experimental leathers as per standard procedures.(Triplicates were carried out for each sample and the average values are reported.

Table III

Recipe of post-tanning process for control and experimental leathers

Process	%	Chemicals	Duration (min)	Remarks
Washing	200	Water	10	
Neutralization	0.75	Sodium bicarbonate	3× 15	pH: 5-5.5
Retannage	100	Water		
	7	Syntan	120	
Fatliquoring	14	Synthetic fatliquor	90	
Dyeing	3	Acid dye brown	30	
Fixing	1	Formic acid	3× 10 + 30	pH 3.5

* - % chemical offer is based on shaved weight of the tanned leather

RESULTS AND DISCUSSION

Experimental leathers treated with 2% Al_2O_3 resulted in garment leathers with higher temperature. Experimental trial resulted in leathers with shrinkage temperature 102°C, whereas control tanning using full chrome resulted in a shrinkage temperature of 105°C. (**Table IV**)

Table IV

Shrinkage temperature of control and experimental tanning processes

Experiment	Shrinkage temperature (°C)
Semi-alum (control)	102 ± 1
Full chrome	105 ± 0.5

Organoleptic properties of crust leathers for experimental and control

Crust leather from both control and experimental processes has been evaluated for various bulk properties by hand and visual evaluation. The average of the rating for the leathers corresponding to experiment has been calculated for each functional property and is given in **Fig. 2.** Higher numbers indicate better property.

The experimental leathers exhibit similar or comparable softness and fullness compared to control leathers. Grain smoothness and general appearance though not higher, are comparable to that of conventionally processed leathers. Overall the performance of both control and experimental leathers are similar.

Physical strength characteristics of crust leathers for experimental and control

It is essential to study the influence of the tanning system on the strength properties of leathers. The physical strength measurements viz., tensile strength, elongation, tear strength, load at grain crack and distension at grain crack were carried out for the control and experimental crust leathers and the data is given in **Table V.** From the table it is observed that full chrome and semi alum crusts leathers showed improved strength properties on par with the standard range for garment leathers.

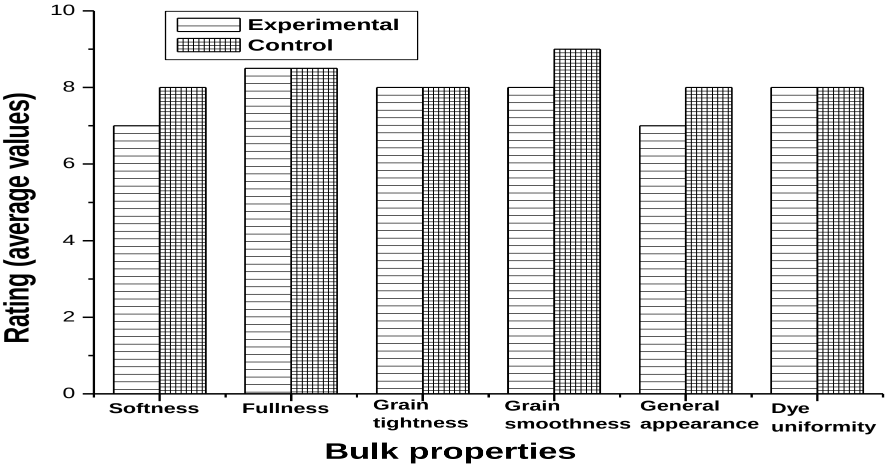


Figure 2: Graphical representation of organoleptic properties of the Experimental and control leather

Table V
Physical strength characteristics of experimental and control crust leathers

Parameter	Experimental (semi-alum)	Control (full chrome)
Tensile strength (Kg/cm^2)	195±20	205±5
Elongation at break (%)	52±0.75	56±1.48
Tear strength (Kg/cm)	49±2	54±5
Load at grain crack (Kg)	25±1	21±1
Distention at grain crack (mm)	12±0.5	13±0.5

Analysis of Spent liquor

The COD, BOD_5 and TDS of the spent liquor for both experimental and control trials were determined and are given in **Table VI**. From the table it is observed that the COD, BOD_5 and TDS of the spent liquor processed using semi-alum tanning system (experimental) are lower than control tanning trial.

Table VI

Characteristic of spent liquor for experimental and control

Experiment	COD(mg/l)	BOD_5(mg/l)	TDS (mg/l)
Semi-alum (Experimental)	111400±2000	14400±1500	64400±2000
Full chrome (control)	128600±2850	25200±1050	92160±1500

Chemical analysis of the crust leather

The chemical analysis of crust leathers from control and experimental tanning trials are given in **Table VII**. The chemical analysis data for the experimental leathers is comparable to the control leathers. However, the water soluble matter for the control leathers is more than the experimental leathers.

Table VII

Chemical Analysis of crust leather of experimental and control

Parameter	Experimental (semi-alum)	Control (full chrome)
Moisture %	13.20	12.50
Total ash content %	2.20	2.80
Fats and oils %	3.10	6.30
Water soluble matter %	3.60	4.50
Hide substance %	51	48
Insoluble ash %	1.4	1.45
Degree of tannage %	54.31	56.77

CONCLUSIONS

The strength and organoleptic properties of the experimental leathers are generally comparable to those of the control leathers. One of the main benefits of our work is the lower environmental impact. The spent tan liquor analysis shows significant reductions in COD, BOD_5 and TDS loads compared to a conventional chrome tannage. Hence, these results suggest that this semi alum tanning system can be used commercially for making garment leather.

REFERENCES

1. Booth, H. The tannage of clothing In Gloving, clothing and special leathers, Tropical Products Institute p 56-57. 1981.
2. Sarkar, K.T. Theory and practice of leather manufacture, published by the author, Neelachal Abasan, Kolkata 700 107, 424-425. 2005.

3. Luo, J. X., Feng, Y. J. and Shan, Z. H., Complex Combination Tannage with Phosphonium Compounds, Vegetable Tannins and Aluminium Tanning Agent. J. Soc. Leather Technol.Chem., **95**, 215, 2011.
4. Madhan, B., Nishad Fathim, N., Raghava Rao, J. et al., Molecular Level Understanding of Tanning Using an Organo-Zirconium Complex. J. Soc. Leather Technol. Chem. **98**, 445, 2003.
5. DasGupta, S., Chrome free tannages: Part 1: Preliminary studies. J. Soc. Leather Technol. Chem.**95**, 188, 2002.
6. Chandrasekaran, B., Rao, J. R., Sreeram, K. J., et al, Chrome tanning: State-of-art on the material composition and characterisation, J. Sci. Ind. Res., , **58(1)**, 1-10, 1999.
7. Rajamani, S., Proceedings on regional workshop on cleaner tanning technologies, 41, 1998.
8. Covington, A. D. and Sykes, R. L.; The use of aluminium salts in tanning, J. Amer. Leather Chem. Ass. **79**, 72, 1984.
9. Covington, A. D.; Tannages based on aluminium (III) and titanium (IV) complexes, J. Amer. Leather Chem. Ass., **82**, 1, 1987.
10. Gaidau, C., Platon, F. and Badea, N.; Investigation into iron tannage, J. Soc. Leather Technol. Chem., **82**, 143, 1998.
11. Sreeram, K. J., Kanthimathi, M., Rao, J. R. et al, Development of an Organo-Zirconium complex – Organozir as possible alternative to chromium, J. Amer. Leather Chem. Ass., **95**, 324, 2000.
12. Covington, A. D. Tanning Chemistry, The Science of Leather, Royal Society of Chemistry, Cambridge, UK. 2009
13. Lampard, G. S. & Covington, A. D. Studies on semi-metal tanning. Journal of the American Leather Chemists Association, **99**, 502-509, 2004.
14. Tuck, D. H. The Manufacture of Upper Leathers. Tropical Products Institute, 56/62 Gray's Inn Road, London, WC1 8LU.Overseas Development Administration. 1981
15. Adewoye, R.O and Rao, J.B. Acacia nilotica –variety adansonii – pods (Bagaruwa) of Nigeria – part I, leather science, vol **24**, 1977
16. Gasmelseed, G. A. and Mulla, T. H. A. Simulation of Continuous Counter-current Leaching of Garad Pods., J. Chem. Biotech., Britain. 1976.
17. McLaughlin, G.D. and Theis, E.R.; The chemistry of leather manufacture, Reinhold Publishing Corp., New York, 133, 1945
18. IUP 2, Sampling, J. Soc. Leather Technol. Chem.**84**, 303, 2000.
19. IUP 6, Measurement of tensile strength and percentage elongation, J. Soc. Leather Technol. Chem. **84**, 317, 2000.
20. IUP 8, Measurement of tear load - double edge tear, J. Soc. Leather Technol. Chem.**84**, 327, 2000.
21. SLP 9 (IUP 9), Measurement of distension and strength of grain by the ball burst test, Official methods of analysis, The Society of Leather Technologists and Chemists, Northampton, 1996.
22. Clesceri, L.S., Greenberg, A.E., Trussel, R.R.; Standard Methods for the Examination of Water and Wastewater, 17th ed, American Public Health Association, Washington DC, 1989.
23. Official Methods of Analysis, the Society of Leather Technologist and Chemists, Northampton, 1965.

IVL O-17

EFFECT OF BINDER SELECTION ON TOPCOAT PROPERTY RETENTION AFTER ACCELERATED WEATHERING

Joseph Hoefler*,Ibrahim Eryazici, Bradley Hageman, Edwin Nungesser, Richard Rosen

Dow Leather Solutions, The Dow Chemical Company, 400 Arcola Road, Collegeville, PA 19426, United States of America, Email: IEryazici@dow.com, BradleyKHageman@dow.com, JHoefler@dow.com, ENungesser@dow.com,RPRosen@dow.com

Within the new car purchasing process, the selection of leather seating is viewed as a premium upgrade over less-expensive alternative options. In keeping with this premium status, leather seating carries with it high expectations for comfort, appearance, and durability. To meet these expectations, Dow Leather Solutions has developed an acrylic topcoat binder with an exceptional balance of performance properties when combined with conventional polyurethane dispersion (PUD) binders. When considering state of the art topcoat systems, however, a continuing unmet need involves retention of properties after seating materials are subjected to a range of accelerated weathering conditions.

This paper compares the performance of fully finished automotive upholstery leathers after they are subjected to a range of accelerated weathering conditions including heat, hydrolysis, and several xenon-arc chamber conditions. A broad range of PUD chemistries and blends of chemistry types were tested, along with an examination of the effect of blending each of these with an acrylic topcoat binder in a standardized upholstery screening formulation. In order to assess performance, measurement of color, gloss, and flexibility were conducted before and after exposure to each accelerated weathering condition.

An examination of the data showed that xenon arc methods using quartz filters resulted in the lowest performance with performance dropping proportionally to the length of the test. An analogous xenon-arc method involving use of an auxiliary lantern and filters was found to result in comparable sample damage, but only after much longer exposure duration. Exposure to hydrolysis and dry heat conditions produced the fewest changes in the samples. The data made evident that certain classes of PUD binders were preferred depending on the weathering specification being considered. Regardless of the various strengths and weaknesses of a particular class of PUD, a strong moderating effect was noted in many PUD-acrylic blend systems. This indicates that the two chemistries produce a measurable synergistic effect when used together in leather upholstery topcoats subjected to accelerated weathering conditions.

1. INTRODUCTION

High performance automotive upholstery leather must meet many stringent original equipment manufacturer (OEM) specifications. These include aesthetic properties such as color, gloss, and touch, as well as flexibility, abrasion resistance, and chemical resistance. These quality control tests are conducted shortly after production, yet the true measure of quality is how well the upholstery performs after many years in service. To ensure that newly manufactured seating can stand the test of time, OEMs also specify a number of tests designed to predict long term durability. The variety of these methods, including exposure to UV light, heat, humidity, and combinations thereof, is partly due to the difficulty in developing a truly predictive accelerated weathering specification (Chomiczewski M et al. 2001).

When considering topcoat binder selection, formulators and tanneries typically choose polyurethane dispersions (PUDs) due to their excellent property balance. The hydrogen bonding across polymer chains and alternating hard-soft morphological domains of PUDs allow them to simultaneously provide high levels of toughness, flexibility down to low temperatures, and minimal tack. The isocyanates chosen to synthesize automotive upholstery PUDs are universally aliphatic, typically isophorone diisocyanate, which supports long-term durability. Conversely, a variety of polyols are used and each has unique strengths and weaknesses with implications for weathering. Polyester polyols often have an excellent cost/performance balance and are not particularly susceptible to UV radiation, but the ester linkages contribute to degradation through hydrolytic cleavage under hot, humid conditions. Polyethers are more resistant to hydrolysis, but are susceptible to UV photooxidation of the ether groups leading to chain scission (Scott 2012). Polycarbonate-based PUDs are more durable than the former types (McGinn and Comes 2013), but usage tends to be limited due to higher cost. An additional complication is that most systems used for upholstery finishing contain more than one class of PUD.

Traditionally, formulators and tanneries have viewed acrylic binders as inferior to PUDs when used for topcoat formulations. This perception is changing, however, as acrylic performance steadily improves. In a recent publication, Dow Leather Solutions introduced a new acrylic particle designed for gloss control and described its enhanced durability over existing PUD based particles (Hoefler et al. 2011). The primary factors studied were aesthetics such as touch, color, and gloss after accelerated weathering. More recently, Dow Leather Solutions reported development of new acrylic binder technology with performance capable of fulfilling typical automotive topcoat requirements (Hoefler et al. 2013). The present study considers the performance after accelerated weathering of not only pure PUD systems of the types mentioned, but also coatings using PUDs blended with this new class of acrylic binder.

2. MATERIALS AND METHODS

Materials:

Leather Preparation – Commercial full-grain automotive crust was cut into 1ft^2 test pieces. A basecoat with the composition shown in Table 1 was applied in two hand sprayed applications at a total wet add-on of 13.0-16.0 grams. The freshly basecoated leather was dried for 4 minutes at 90°C after each coating. The pieces were stored overnight to facilitate complete curing and were smoothed afterwards at 135°C using a Finiflex ironing machine. A topcoat (as shown in Table 2) was then spray-applied in two applications to a total dry add-on of 2.0-2.5 grams. The topcoats were dried for 2 minutes at 90°C between applications and again for 4 minutes after final coating.

Table 1: Basecoat Formulation

Material	Parts
Water	200.0
Black pigment dispersion	120.0
Softening agent	150.0
Polyurethane resin 1	320.0
Polyurethane resin 2	80.0
Acrylic resin	100.0
Matting agent	90.0
Performance silicone	10.0
Urethane thickener	4.2
Total	1074.2

Table 2: Topcoat Formulation

	Formulation with PUD	Formulation with PUD and acrylic
Material	**Parts**	**Parts**
Water	245	245
Unbound duller (no binder)	294	294
PUD binder	286	143
Functional acrylic binder	---	143
Flow agent	10	10
Performance silicone	70	70
Black pigment dispersion	15	15
Polymeric isocyanate	80	80
Urethane thickener	25-30" on a #2 ZAHN cup	
Total	1000	1000

The finished leather was allowed to cure for at least 5 days at ambient conditions and then cut into smaller pieces and subjected to accelerated weathering processes.

Methods:

Sample Testing Workflow - The present study explores a number of binder variables in the context of coating performance after accelerated weathering. A variety of polyurethane dispersion binders were used including polyester, polyether, and polycarbonate polyol chemistries, as well as blends of polyester and polycarbonate polyols. Multiple examples of each polyol type were tested in order to provide averages of performance, but the conclusions drawn can not necessarily be extended beyond the specific binders tested.

In addition to variations in the PUD binder, an acrylic binder designed for use in leather topcoats was substituted for 50% of the binder solids in a number of experiments. This was done in order to test the effect on performance of a combined PUD/acrylic topcoat system after accelerated weathering.

After application of the leather finishes, leather swatches of each topcoat were subjected a variety of accelerated weathering methods comprising:

- SAE J-2412: A method which involves high heat and exposure to UV and visible light generated by a xenon arc within a controlled irradiance chamber. The method also includes a dark cycle at high humidity conditions. This method was run at an irradiance level of 225 kJ/m^2.

- FLTM BO 116-01: A related method which utilizes auxiliary glass panels designed to filter light below a wavelength of 335nm. Exposures using this method were conducted at levels of 225 and 976 kJ/m^2.
- Dry heat: Exposure to heat was accomplished by placing the samples in an oven at a temperature of 90°C for 500 hours.
- Hydrolysis-producing conditions: Hydrolysis was promoted by placing the samples in a controlled humidity chamber at a temperature of 50°C and 95% relative humidity for 500 hours.
- A control sample stored at ambient conditions

After exposure, the leather samples were evaluated for change in gloss, color stability, and Bally flexibility. Additional details related to weathering and leather test methods may be found below.

<u>UV Exposure</u> - Samples were cut into 14.0 x 6.5 cm test strips and placed in an Atlas Ci5000 WEATHER-OMETER (Atlas corporations, Mount Prospect, Illinois).

<u>Hydrolysis Exposure</u> – Similar-sized leather test strips placed in a Stability Environments model 33HR-S1 hotpack (SEI, Inc., Warminster, PA) set to maintain 50^{o}C/95% relative humidity for 500 hrs.

<u>Thermal Exposure</u> – Similar-sized leather test strips placed in a model 1350FSM forced draft oven (VWR Scientific, Radnor, PA USA) set at 90^{o}C for 500 hrs.

After the exposures were completed, samples were removed from the chambers and allowed to equilibrate at ambient conditions for at least 1 day before testing.

<u>Gloss</u> – Measured at 60^o with a BYK-Gardner Micro-TriGlos (part# 5420). Each sample was measured in triplicate. After the completion of accelerated weathering, gloss measurements of weathered and control samples were compared in order to calculate a ratio indicative of gloss stability. This method allowed normalization of different initial gloss levels and focuses only on changes to gloss, where a result of “1” indicates no change in gloss after weathering.

<u>ΔE (Color difference)</u> – CIE L*a*b* color was measured using a X-Rite spectrometer Model Ci7 (X-rite, Grand Rapids MI). Conditions used were D65/10 degree observer with a 25mm aperture. An unexposed sample was used as the control in order to allow calculation of a ΔE value.

<u>Bally Flexibility</u> - Samples were cut into 6.5 x 3.8 cm test strips and subjected to flex testing using a Bally flexometer (Otto Specht, Stuttgart, Germany, Model 739). After either 5,000 or 100,000 flexing cycles at ambient conditions, the leather was evaluated using a stereomicroscope at 45x magnification to assess damage to the topcoat finish such as cracking and crazing. A rating of 1-10 was applied to each of the samples depending on the extent of the damage to the topcoat. A rating of 1 indicates severe damage, while a rating of 10 indicates no damage after flexing.

3. RESULTS AND DISCUSSION

Gloss Evaluation of Weathered Systems:

Figure 1 shows average normalized gloss levels for pure PUD and mixed PUD/acrylic systems as the exposure method was changed. In general, the data shows that the exposure methods involving UV exposure resulted in the largest gloss changes, while oven and hydrolysis chamber exposure produced small changes. At equal irradiance levels, the modified wavelength distribution of the Ford method resulted in minimal gloss changes when compared to the SAE J-2412. However, when the irradiance under the Ford method was tripled, much larger gloss changes were observed, indicating that in this case the milder spectral light distribution delayed, but did not prevent, coating degradation.

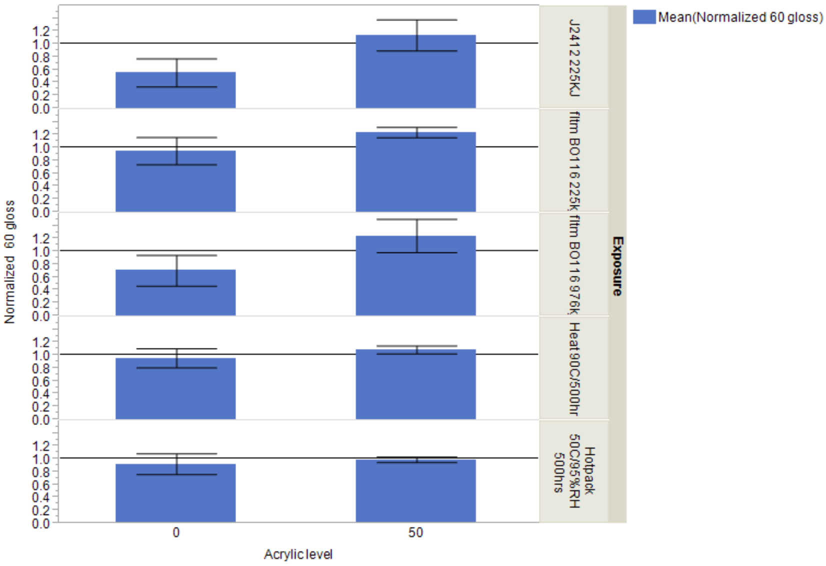


Figure 1: Normalized 60° Gloss Averages by Exposure Type

A comparison was also made between the performance of topcoats containing solely PUD binders versus a 50:50 blend of PUD and acrylic binders. After exposure to the J-2412 test, a system of combined PUD/acrylic polymer types manifested improved performance over pure PUD, with an average normalized gloss level much closer to 1.0. In all cases, the addition of the acrylic binder resulted in at least comparable performance. An additional beneficial effect of adding acrylic content was that the standard deviation of many of the gloss measurement averages decreased, indicating more consistent, predictable performance after weathering.

A more detailed view of the data is shown in Figure 2, where normalized gloss performance is shown for each type of PUD chemistry. Here the same trends as described in Figure 1 are visible, but additionally, the various strengths and weaknesses of individual PUD chemistries are apparent. The polyester-based PUD type, in particular, showed comparatively poor performance, especially in the oven and hydrolysis chamber tests. The best performance was observed in the case of the polycarbonate PUDs, which manifested only slight gloss changes after each of the weathering methods employed. An additional observation was that the PUD binders containing a combination of polyether and polycarbonate polyols tended to show the weaker performance of the pure-polyether systems, rather than a compromise between the two pure systems.

The beneficial effect of adding acrylic content to the topcoat systems was observed in the case of the polyester, polyether, and mixed polyether/polycarbonate PUDs. In almost every case, the normalized gloss of the blended systems was closer to “1”, showed lower experimental scatter, or both.

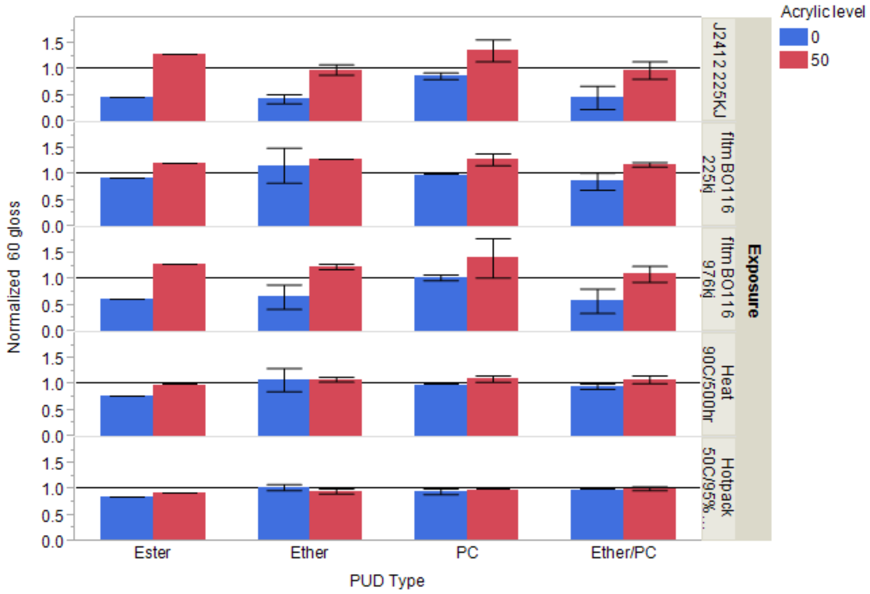


Figure 2: Normalized 60° Gloss by Binder and Exposure Type

Color Stability of Weathered Systems:

Colorimetry data was also collected for both the unexposed and exposed samples and reported as a delta E value, as shown in Figure 3. Once again, the samples underwent the most change after exposure to xenon discharge weathering methods, with delta E values in excess of 2.0 being recorded. The performance was again very similar when comparing the SAE method at 225kJ of exposure and the Ford method at 976kJ, although significantly less color change was recorded when the Ford method was run at a 225kJ exposure. When the samples were exposed to the heat and hydrolysis conditions, only minimal changes were noted. As with the gloss measurements, increased stability was observed in the coatings using PUD/acrylic blended polymer chemistries, with several delta E levels being reduced by approximately 50% and in no case were the delta E measurements higher in an acrylic-containing sample. Similar or lower standard deviations were also seen in the acrylic-containing topcoats.

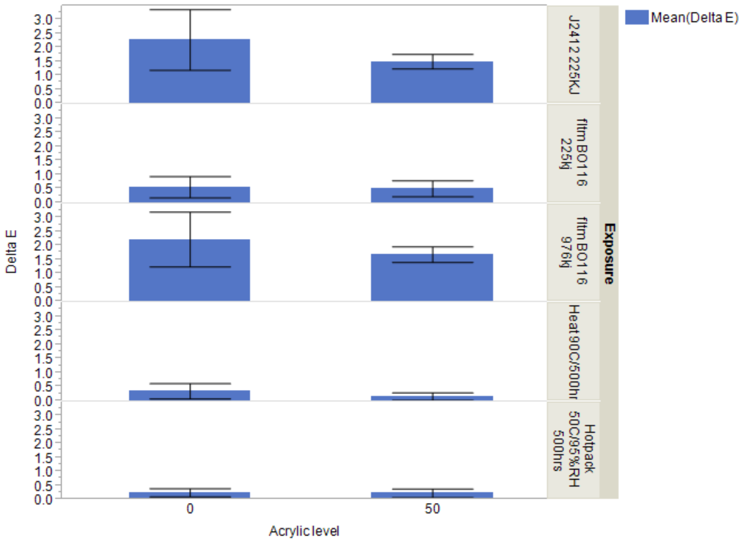


Figure 3: Delta E Averages by Exposure Type

A more detailed look at the colorimetry data is provided in Figure 4, where performance as a function of PUD type is provided. Here, the generally poor performance of the polyester-type PUD is shown, especially after heat and humidity exposure, although relatively poor performance after UV exposure was also demonstrated. As shown when considering gloss change, the polycarbonate was clearly the best performing class in terms of color stability. As shown previously, preparing a mixed polyether/polycarbonate PUD largely resulted in reproducing the weaker performance of the pure polyether binder rather than performance in between that of the two pure types.

Addition of acrylic content to the topcoat systems had the largest effect when the weakest PUD types were used. In many of those cases, the introduction of the acrylic polymer improved performance noticeably. This effect was most readily seen after UV weathering by the SAE and Ford methods when the polyether/polycarbonate blend was used and in the case of the polyester type after oven and hydrolysis chamber exposure.

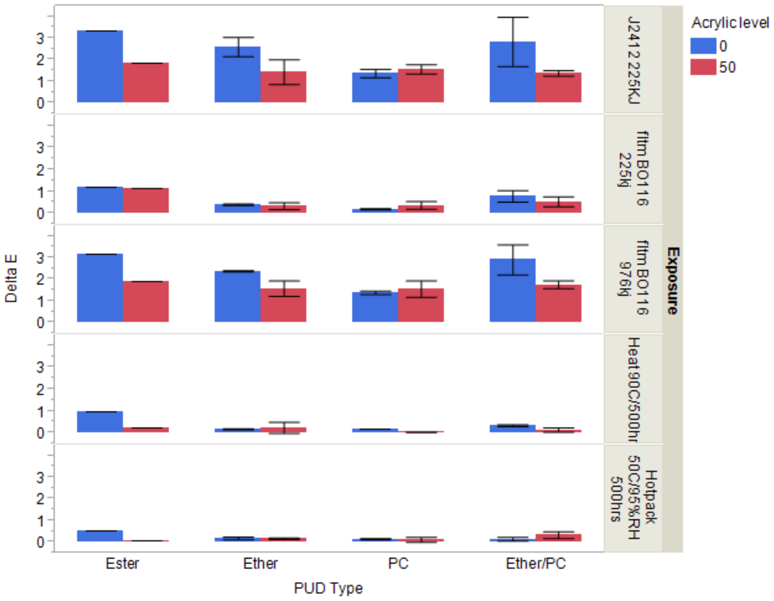


Figure 4: Delta E by Binder and Exposure Type

Bally Flexibility of Weathered Systems:

In addition to appearance measures, the flexibility and softness of leather articles is often negatively impacted by weathering processes. In order to assess this property, the Bally flexibility test was run on the samples produced for this study. While the standard specification calls for 100,000 flex cycles, many of the weathering conditions led to catastrophic failures after this large number of flexes. In order to better assess the relative performance of all of the experimental systems, the much less demanding level of 5,000 cycles was also selected.

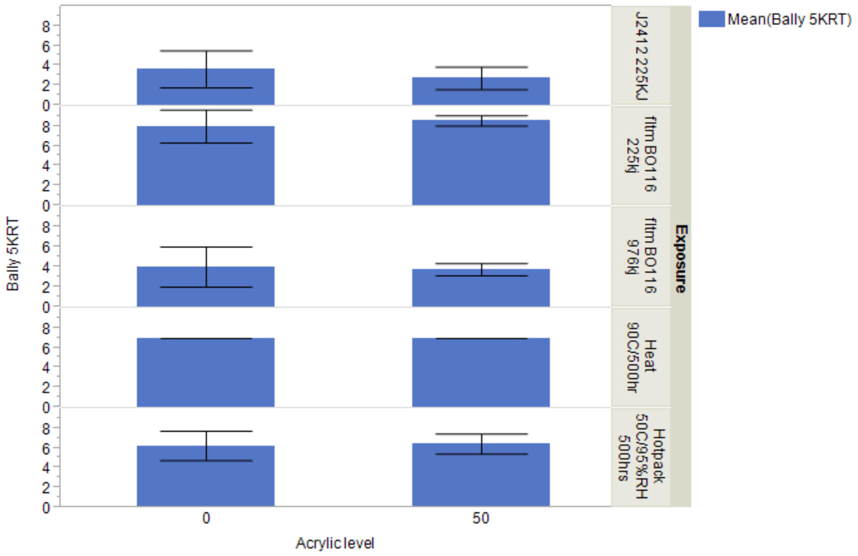


Figure 5: Bally Flex (5,000 Cy) Averages by Exposure Type

As shown in Figure 5, the samples exposed to 225 KJ of energy using the SAE J-2412 method underwent the most dramatic changes, manifesting a large increase in embrittlement. By contrast, the Ford BO-116 method at the same irradiance level showed almost no change, indicating the light-filtering effect of the bandpass filters in the lantern. When the irradiance level of the Ford test was increased to 976KJ, a more noticeable decrease in performance was observed, however, performance was still higher than after testing using J-2412.

When considering aging in dry heat conditions, the trends observed when testing gloss and color were maintained. The average performance was high at the test level of 5,000 cycles. Similarly, only a small loss of performance was observed after exposure in the hydrolysis chamber.

The results averaged across PUD types did not show a measurable improvement in flexibility based on the presence of the acrylic binder. However, performance was also not harmed by the acrylic addition.

When considering the performance of individual PUD types as shown in Figure 6, it can be shown that performance was similar across PUD types after 5,000 flexes. A notable exception was in the case of the polyester PUD, which suffered a significant loss of flexibility after hydrolysis. Another observed trend was that the polycarbonate PUDs retained the most flexibility after being exposed to the solar testing methods.

Figure 6 also shows the effect of acrylic polymer addition to the experimental systems. These data indicate that the acrylic effect was most beneficial when added to the polyester and polyether/polycarbonate blended PUD. In those cases, it tended to improve hydrolysis and UV weathering resistance.

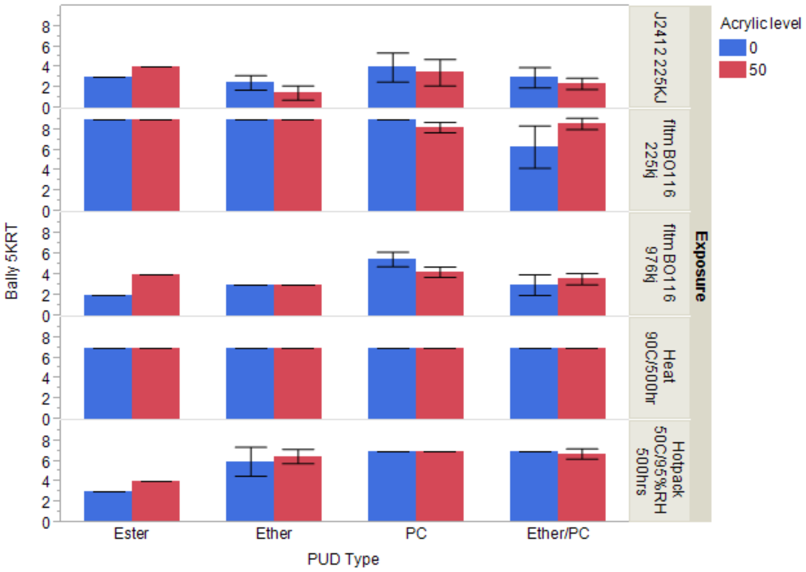


Figure 6: Bally Flex (5,000 Cy) Results by PUD and Exposure Type

A second set of Bally tests evaluated performance of the samples after 100,000 room temperature cycles. Due to extensive cracking, none of the samples exposed to 225 kJ using J-2412 or 976 kJ using the Ford method were evaluated after 100,000 cycles and are omitted from Figure 7, below. However, at the same 225KJ exposure level using the Ford test, a measure of performance was retained. Exposure of the samples to both heat and hydrolysis conditions produced modest decreases in performance.

Addition of acrylic polymers to the experimental systems modestly improved performance when exposed using the Ford method and had no negative consequences in the other cases.

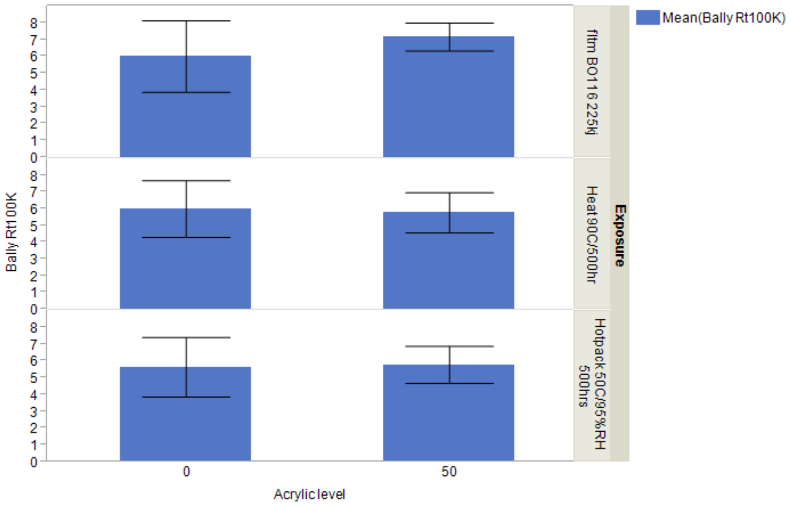


Figure 7: Bally Flex (100,000 Cy) Averages by Exposure Type

Concerning the performance of specific PUD chemistries in Figure 8, these data indicated that the polyester-containing PUDs tested showed lower overall performance than the polyester- and polycarbonate-containing polymers, with polycarbonate PUDs manifesting the best performance. The polyester composition primarily showed weakness after oven and hydrolysis chamber aging. As discussed above, the polyether/polycarbonate binder had UV resistance worse than either of the pure compositions.

Addition of acrylic polymers to these systems was beneficial in improving flex performance after exposure using the Ford method, especially when using polyether PUDs. The heat and humidity resistance properties of the polyester backbone were also improved by addition of acrylic polymer.

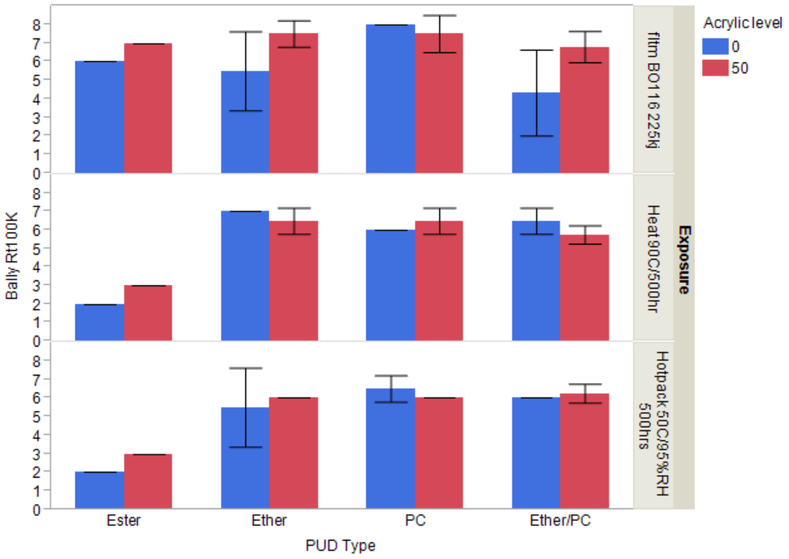


Figure 8: Bally Flex (5,000 Cy) Results by PUD and Exposure Type

4. Conclusions

A study was undertaken to examine the performance of topcoat formulations as the PUD and acrylic binder composition was systematically varied. The finished leather samples were exposed to accelerated weathering methods involving UV, heat, and humidity exposure and then tested for gloss and color stability as well as flexibility. An analysis of the data allowed a number of conclusions to be drawn:

With regard to the exposure conditions, the most rigorous were the xenon methods, which included UV light in addition to heat and humidity. This is not surprising in that UV light is known to produce chain scission and radical generation in a number of coating systems in addition to chain degradation brought about by hydrolysis (Scott 2012; Hunter 2000). Furthermore, heat exposure may induce stiffening of films due to loss of plasticizing solvents and hydrolysis due to generation of water through thermal oxidation (Levantovskaya 1971). The Ford BO 116-01 method was found to be less destructive than the SAE J-2412 method at equal irradiance. When the irradiance under the Ford method was increased to three times the irradiance of the SAE method, the performance was found to be similar across both methods. This effect is thought to be due to the long-wavelength bandpass filters used with the former method, which filters out wavelengths shorter than 335nm. When compared to natural sunlight, the J-2412 method supplies an unnaturally high irradiance of these short UV wavelengths which leads to destructive photochemistry in many polymers (Chomiczewski

2001). The filters employed under the Ford method sharply reduce the intensity of these wavelengths.

Exposure of the polyester polymers under conditions of heat and humidity consistently led to significant loss of performance. This is attributed to the tendency of the ester linkages to undergo hydrolysis under humid conditions. Oven aging can also lead to hydrolysis as described by Levantovskaya (1971) as hydrogen peroxide formed through thermal oxidation decomposes, producing water molecules.

In further considering polymer chemistry, the polycarbonate class of PUDs was shown to consistently demonstrate the best balance of properties in gloss and color stability as well as retention of flexibility. The relatively high expense of this class of PUDs has often led formulators to choose a different chemistry or minimize the polycarbonate content. Minimization of polycarbonate may be accomplished through use of auxiliary binders of a different composition or a single product utilizing a polycarbonate blended with a different class of polyol. The use of these mixed polyol systems may not be an effective solution if weathering resistance is a desired property. This study showed that in many cases, PUD systems containing both polyether and polycarbonate polyols did not have performance in between the two pure systems, but instead tended to perform like the weaker component.

One subject of particular interest was the effect of combining PUD and acrylic binders. Traditionally, formulators and tanneries have been reluctant to incorporate acrylic polymers in high performance automotive topcoats since a very high PUD content was regarded as necessary in order to achieve the stringent performance requirements. This study showed a significant acrylic binder fraction may be used without a performance penalty when considering the properties studied. In fact, in many systems, addition of 50% acrylic binder solids had the effect of improving performance, including flexing performance. Acrylic polymers were especially effective at improving overall UV weathering performance and also the hydrolysis resistance of polyester PUDs.

5. References

1. Chomiczewski M, et al., *Technical Briefing: New Automotive Interior Test Methods*. Atlas Electrical Devices Co. 2001. pp. 26-27, 35.
2. Scott G, *Atmospheric Oxidation and Antioxidants*. Elsevier. 2012. p. 388.
3. McGinn A, Comes V, Aliphatic Polycarbonate Polyurethanes with Broad Chemical Resistance for In Vivo Medical Devices [http://www.mddionline.com/article/chemical-resistance-and-stress-cracking-polyurethanes] para 5-6
4. Hoefler J, Chung C, Hageman B, and Lafleur E, Novel Acrylic Particle Technology. *JALCA* 2011, 106(11), pp. 316-325.
5. Hoefler J, Hageman B, Chung C, Smith R, High Performance Acrylic Polymer Technology Use in Leather Finishing Processes. *JALCA* 2013, 108(8), pp. 311-317.
6. Hunter L, White J, Cohen P, Biermann P, A Materials Aging Problem in Theory and Practice. *Johns Hopkins APL Tech. Digest* 2000, 21(4), p. 575.
7. Levantovskaya I, Barshtein R, Yazvikova M, Gorbunova V, Kovarskaya B, The role of hydrolytic processes during thermal oxidation of polyester plasticizers. *Polymer Science U.S.S.R.* 1971, 13(4), p. 1969.

ENZYMATIC UNHAIRING: PERMEABILITY ASSAY OF BOVINE SKIN EPIDERMIS WITH FUNGAL ENZYME EXTRACTS

Galarza Betina*, Garro Laura, Cortizo Lorena, Greco Carlos, Hours Roque

Research Center for Leather Technology (CITEC), National Institute of Industrial Technology; Scientific Research Commission of Province Buenos Aires (INTI-Cueros; CICPBA), Camino Centenario e/505 y 508, (1897) Gonnet, Argentina, betinagal@hotmail.com, mariagarro12@gmail.com

Research and Development Center for Industrial Fermentations (CINDEFI, CONICET, UNLP); School of Science, National University of La Plata, 47 y 115, (B1900ASH), La Plata, Argentina, hours@biotec.org.ar

The aim of enzymatic unhairing is allow the separation of the outer sheath of hair root from the dermal connective tissue. It’s considered an ecofriendly process. It’s not necessary more expensive since if it’s applied on the epidermis surface enzymatic extracts could be saved. The purpose of this work was to analyze the changes in pilosebaceus unit, basal lamina by unhairing enzyme action. Various keratinolytic fungi, previously isolated and selected from different soil samples were used: Neurospora crassa, Verticillum albo-atrum, Trichophyton ajelloi, Chrysosporium sp, Aspergillus sidowii, Paecilomyces lilacinus and Acremonium murorum. Fungal isolates were cultivated in solid state conditions using hair waste obtained from the hair-saving unhairing process as substrate. Enzyme extracts were characterized according to their keratinolytic and proteolytic activity and protein content. Bovine skins were placed in plastic plates where the epidermis contact with different solutions: fungal enzyme extracts with commercial tensioactives (0.1%, 0.5%), biocide 0.2% w/w (wet skin) for 4 h (soaking) and 24 h (unhairing) at 25°C and 40 rpm. Samples of skin with and without enzymatic treatment were fixed in 4% formaldehyde, dried on increasing concentration of ethanol and analyzed with scanning electron microscopy. It was observed that the enzymes altered the epidermis, where detachment of corneocytes and empty hair follicles were observed. Characteristic patterns of hair cuticle and collagen fibres were preserved in skin control with buffer. The strongest depilatory effect was observed in Trichophyton ajelloi. It was concluded that the enzyme penetration through epidermis could provide beneficial effect for the application of reagents during the handcrafted tanning of leather.

Keywords: unhairing, keratinolytic fungal enzymes, permeability, epidermis

1. INTRODUCTION

The epidermis is a keratinized stratified squamous ephithelium derived from ectoderm and is the outermost layer of the skin. The cells of this layer are categorized into two major groups: keratinocytes and nonkeratinocytes. The epidermis layers can be classified from the basement membrane to the outer surface as follows: stratum basale (basal lamina), stratum spinosum (spinous or prickle layer), stratum granulosum (granular layer), stratum lucidum (clear layer) and stratum corneum (horny layer) (Monteiro-Riviere 2006).

In bovine skin the main barrier for substances is located in the upper layer, stratum corneum. To allow enzymes reach the pilosebaceous unit and basal lamina without collagen damage, they should diffuse through the epidermis involving transport across a series of resistances (Gupta 2012). These are crucial elements for the design of an unhairing system. Trabitzsch (1966) refers the technical and operational conditions for the loosening of hair, and indicates that even though corium (dermis) is thicker than epidermis (grain layer), enzymes diffuse faster through dermis (Cantera et al. 2004).

Stratum corneum keratin acts as a barrier, in this layer there is a continuous sheet of cells rich in protein (corneocytes) embedded in an intercellular matrix of lipids. These cells are highly organized and stacked one upon another to form vertical interlocking columns with a flattened tetrakaidecahedron shape that provide a minimum surface: volume ratio. The transepidermal water loss is a function of the integrity and permeability of this layer because of this special arrangement, typical of hairy skin. Also in recent years follicular penetration processes have been considered. More recent studies strongly suggest that skin appendages play an important role in penetration processes of substances (Knorr et al. 2009).

For enzyme diffusion, it is necessary to generate channels through this barrier to allow the enzymes to reach the pilosebaceous unit. Ideal enzyme unhairing will be achieved when proteolytic activity is directed towards basal lamina and pilosebaceous unit with minimal effect on collagen producing as a result a good quality of leather.

The changes of epidermis and the generation of routes more accessible for enzyme diffusion would let unhairing substances reach the basal lamina, minimizing in this way undesirable activity on collagen like when enzymes diffuse across the corium (dermis).

The objective of this research was to analyze the penetration of fungal enzymes, tensioactives and biocide through bovine epidermis to reach pilosebaceous unit and basal lamina evaluating morphological changes and depilatory effect by scanning electron microscopy.

2. MATERIAL AND METHODS

Fungal strain isolates: cultures and characterization

Strains were isolated from alkaline-calcareous, neutral and alkaline-sodium soils (Elíades et al. 2010). Then fungal strains were screened in order to determine their ability to produce keratinolytic enzymes using Keratin Azure (Sigma K-8500) as substrate (Scott et al. 2004; Cantera et al. 2003).

Neurospora crassa, Verticillum albo-atrum, Trichophyton ajelloi, Chrysosporium sp, Aspergillus sidowii, Paecilomyces lilacinus, Acremonium murorum were the selected fungal strains.

Fungal crude enzyme extracts (**CE**) were obtained by solid state culture in hair waste substrate from the hair-saving unhairing process as described by Galarza et al. (2004). They were characterized according to their keratinolytic and proteolytic activities and protein content in presence of biocide and tensioactives.

Tensioactives used were: Isogras AN: ethoxylated fatty alcohol, anionic, used in soaking; Baymol AZ: non-ionic tensioactive, free of nonylphenol and nonylphenol-ethoxylates, used in unhairing step.

Biocide´s solution used was: (Thiocyanomethylthio)benzothiazole (TCMTB) 27%, N,N-Dimethylethylamine (penetrating/emulsify) 10%, cresol 63% (FUBA Chem).

CE from selected fungi (CE) were tested in a permeability assay in the soaking and unhairing steps.

Assessment of protein content and proteolytic activity

Protein concentration was determined by Bradford's method (Bradford 1976).

Assay of proteolytic and keratinolytic activities

Azocaseinolytic activity was determined using azocasein as substrate (sulphamide azocasein, Sigma Chem.Co., St. Louis, MO). Reaction mixture containing 100 µl of crude extract and 250 µl of the 1% (w/v) substrate solution in 0.1 M Tris-HCl buffer pH 9, Isográs AN 0.1% 50 µl and Baymol 0.,5% µl was incubated for 30 min a 37°C, stopped by addition of 1 ml trichloroacetic acid (TCA) 10% (w/v) and centrifuged (3000xg, 15 min). One ml of NaOH was added to 0.9 ml of the supernatant, agitated and measured at 440 nm (triplicate). Blank was performed using enzyme solution inactivated for heating at 100°C, 5 min (Liggieri et al 2004). Azocasein activity unit (Uazoc) is defined as the amount of enzyme that, under the test conditions, causes an increase of 0.1 Abs440nm per minute.

Keratinolytic activity was assayed by using hair waste as substrate (washing with tensioactives, dried at 45°C, ground, autoclaved at 121°C and retained with 850 µm sieve, USA Standard ASTM E 11-61).

Reaction mixture containing 150 µl of CE and the 1%(w/v) substrate in buffer Tris-HCl 0.1 M, pH 9 (Yamamura et al. 2002), Isogras AN 0.1% 50 µl , Baymol AZ 0.5% 50 µl and biocide TCMTB (relation biocide/enzyme (w/w): 100 µg biocide/1 µg CE protein) was incubated at 37°C in agitation (100 rpm) for 60 min. Reaction was stopped by addition of 1 ml of trichloroacetic acid (TCA) 10% (w/v), centrifuged (5000xg 15 min) and the supernatant was measured at 280 nm (triplicate). Reaction blanks were performed by incubation 60 min: substrate, tensioactives and buffer. After that CE, biocide and TCA 10% (w/v) were added and procedure was the same as before. Keratinolytic activity unit (Uk) was defined as the amount of enzyme that, under the test condition, causes an increase of 0.01 Abs280nm per minute.

Permeability assay of bovine skin epidermis with fungal enzyme extracts

Fresh bovine skin from the butt was placed in plastic plates of 26 cm length and 14cm width with 8 wells of 5 cm diameter and 20 ml volume (Fig. 1). These plates allow the contact between epidermis and substances without spilling. The skin was held up horizontally with wooden boards of 20 cm length and 2 cm width and tightened with fixing nuts and placed on orbital shaker. The wells with circular shape allowed watertight compartments to test different solutions (Figs.2 and 3) (Garro 2012).

Soaking step: Each well was filled with 8 ml of different CE, Isogras AN 0.1% w/v and biocide (0.2% w/w wet skin) (duplicate). Incubation was done during 4 h at 25°C with agitation (40 rpm).

Unhairing step: Baymol AZ 0.5% was added in each well after soaking. Incubation 48 h at 25°C, agitation 40 rpm.

Control wells: I.- 8 ml buffer Tris-HCl 0.1 M pH 9 and biocide (0.2% w/w wet skin); II.- 8 ml buffer Tris-HCl 0.1 M pH 9, Isogras 0.1% p/v, Baymol 0.5% and biocide (0.2% w/w wet skin); III.- fresh skin without incubation.

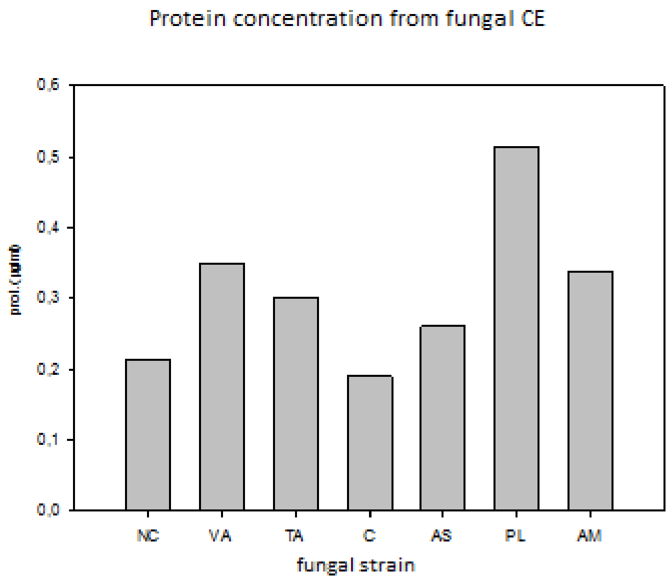
After treatments, samples of skin from each well were fixed 2 h and postfixed for 24 h in 4% formaldehyde, dehydrated in 30%, 50% and 70% ethanol with three changes of 15 min in each. The day of microscopic analysis one change of 100% ethanol was made. After this, samples were treated by critical point drying, mounted and metalized prior to the examination by scanning electron microscope (FEI-Quanta 200, LIMF Laboratorio de Investigaciones de Metalurgia Física, Facultad de Ingeniería, UNLP, Argentina)

Fig. 1.- Permeability assay: plastic plates holding bovine skin

Fig. 2.- Plastic plates.

Fig. 3.- Wooden boards.

3. RESULTS AND DISCUSSION



References

Neurospora crassa (NC)

Verticillium albo-atrum (VA)

Trichophyton ajelloi (TA)

Chrysosporium sp [C]

Aspergillus sidowii (AS)

Paecilomyces lilacinus (PL)

Acremonium murorum (AM)

Paecilomyces lilacinus (PL) rorum

Fig. 4. Protein concentration in different fungal CE

Paecilomyces lilacinus CE showed the highest protein concentration (0.514 µg/ml) whereas the lowest value was found with Chrysosporium CE (0.190 µg/ml) (Fig.4). Both strains have been reported as proteolytic genera; even so Chrysosporium have reported keratinophilic activity (Wilson et al. 2007; Khan et al.2003).

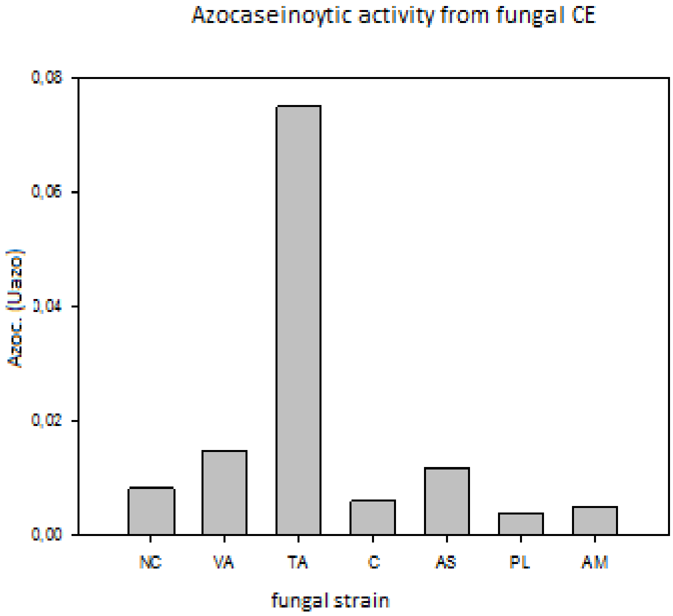


Fig.5. Azocaseinolytic activity in different fungal CE

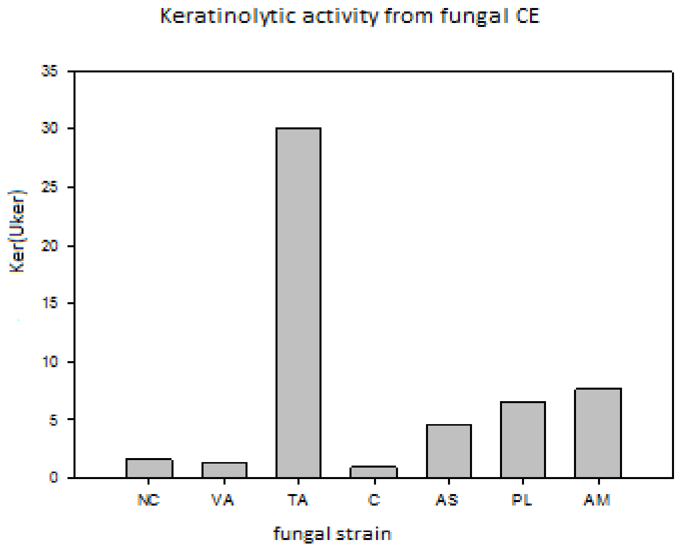


Fig.6. Keratinolytic activity in different fungal CE

Trichophyton ajelloi produced a CE with the highest enzymatic activities (proteolytic and keratinolytic): 0.075 Uazo and 30.1 Uker (Fig.6). This in accordance with "dermatophyte" taxonomic classification. Althougt this fungal strain is not pathogenic towards human or animals, keratinases are expressed. "Sulphytolisis" is the mechanism whereby filamentous fungi break down insoluble keratin by keratinases (Kunert 2000).

SEM observation

The morphological changes were observed by scanning electron microscope. Control skin with buffer and biocide had hair cuticle preserved (Fig.7). CE from Neurospora crassa, Chrysosporium sp, Aspergillus sidowii and Paecilomyces lilacinus (Fig.9) did not cause any effect in skin epidermis. In Verticillum albo-atrum and Acremonium murorum (Fig.8 and 10) a detachment of corneocytes have been found. CE action of Trichophyton ajelloi displayed empty hair follicles, stratum corneum with normal characteristics and collagen fibers with typical pattern (Fig.11.1-11.2).

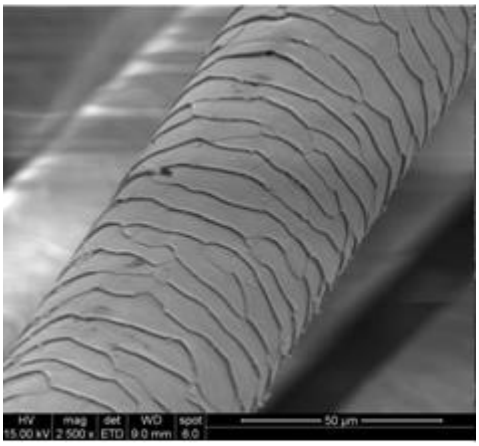


Fig.7 Control: buffer and biocide: hair cuticle preserved 2500 x

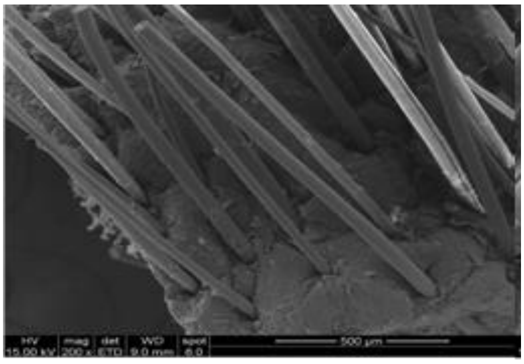
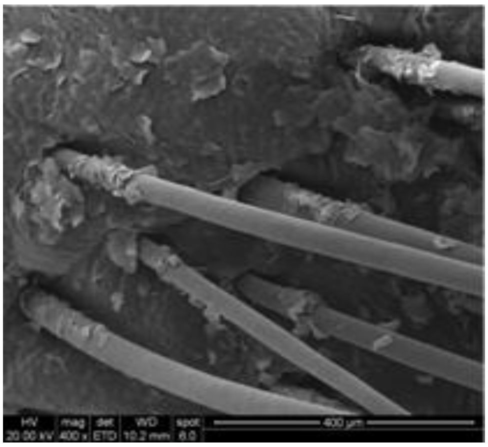


Fig.8. Verticillum albo-atrum(VA): corneocytes detached 400x

Fig. 9. Paecilomyces lilacinus (PL): hair and epidermis with normal characteristics 200 x



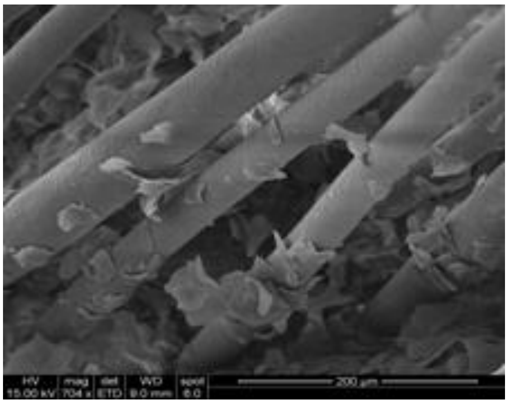
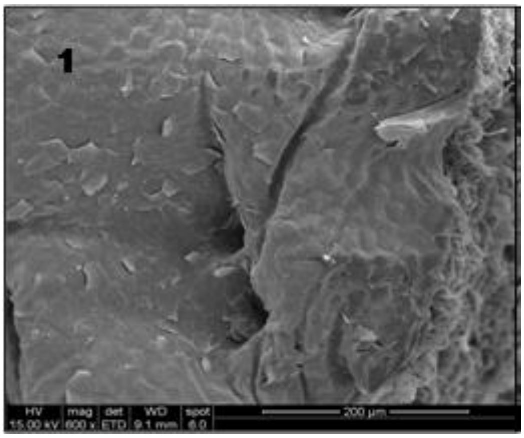


Fig.10 Acremonium murorum (AM): detached corneocytes 704x

Fig.11.1 Trichophyton ajelloi (TA) (1): empty hair follicles, stratum corneum with normal characteristics, 600 x



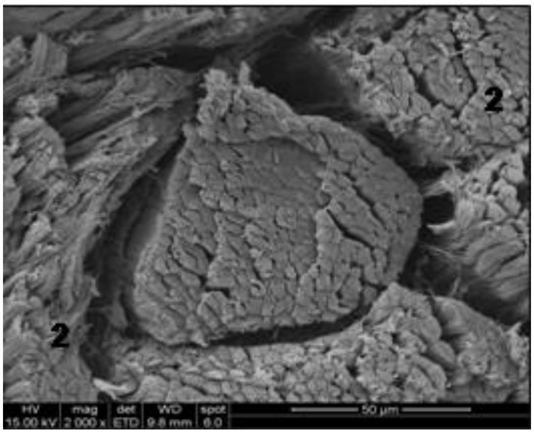


Fig 11.2 Trichophyton ajelloi (TA) (2): collagen fibers with characteristic pattern 2000 x

4. CONCLUSIONS

Correspondence of enzyme activity and depilatory effect was found in Trichophyton ajelloi CE, although the action was lower than other assays with immersed skin (Galarza et al. 2016).

Finally, it was concluded that the enzyme penetration trough epidermis could provide beneficial effects for the application of reagents during the handcrafted tanning of leather.

5. REFERENCES

Bradford M, A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding, Analytical Biochemistry, 1976, **72**, 248-254.

Cantera CS, Garro ML, Goya L, Barbeito C, Galarza B, Hair saving unhairing process: part 6, stratum corneum as a diffusion barrier: chemical-mechanical injury of epidermis, Journal of the Society of Leather Technologists and Chemists, 2004, **51**, 121-131.

Cantera CS, Goya L, Galarza B, Garro ML, López LMI, Hair saving unhairing process. Part 5. Characterization of enzymatic preparations applied in soaking and unhairing processes, Journal of the Society of Leather Technologists and Chemists, 2003, **87**, 69-77.

Elíades L, Cabello M, Voget C, Galarza B, Saparrat M, Screening for alkaline keratinolytic activity in fungi isolated from soils of the biosphere reserve "Parque Costero del Sur", World Journal of Microbiology and Biotechnology, 2010, **26** (11), 2105-2011.

Galarza B, Garro ML, Martegani J, Hours R, Characterization and evaluation of a fungal enzymatic pool with unhairing activity, Journal of the Society of Leather Technologists and Chemists, 2016, **100**, 257-262.

Galarza BC, Goya L, Cantera C, Reinoso H, Fungal biotransformation of bovine hair. Part I: isolation of fungus with keratinolytic activity, Journal of the Society of Leather Technologists and Chemists, 2004, **88**, 3, 93-98.

Garro ML, Tesis, Depilado enzimático conservador del pelo: injuria química y mecánica de la epidermis para incrementar los procesos difusivos, 2012, http://sedici.unlp.edu.ar/handle/10915/27451).

Gupta RC, Veterinary Toxicology Basic and Clinical Principles, 2° edition, Academic Press, 2012, 338.

Khan A, Williams K, Molloy M, Nevalainnen H, Purification and characterization of a serine protease and chitinases from Paecilomyces lilacinus and detection of chitinase activity on 2D gels, Protein Expression and Purification, 2003, **32**, 2, 210-220.

Knorr F, Lademann J, Follicular transport route: research progress and future perspectives, European Journal of Pharmaceutics and Biopharmaceutics, 2009, **71**, 173-180.

Kunert J, Physiology of keratinophilic fungi. Revista Iberoamericana de Micologia, RKS Kushwaha & J. Guarro, Bilbao, 2000, **10**, 77- 85.

Liggieri C, Arribère MC, Trejo S, Canals F, Avilés F, Priolo N, 2004. Purification and biochemical characterization of Asclepain c I from the latex of Asclepias curassavica, The Protein Journal, 2004, **23**, 403-411.

Monteiro-Riviere N, Integument, Dellmann´s 6°edition, Textbook of Veterinary Histology, 2006, chapter 16, 320-349.

Scott J, Untereiner W, Determination of keratin degradation by fungi using keratin azure, Medical Micology, 2004, **42**, 239-246.

Trabitzsch H, Concerning the possibility of wmploying enzyme in the beamhouse, Journal of the Society of Leather Technologists and Chemists, 1966, **50**, 382-389.

Wilson A, Dodson HI, Janaway RC, Pollardà AM, Tobin DJ, Selective biodegradation in hair shafts derived from archaeological, forensic and experimental contexts. British Journal of Dermatology, 2007, **157**, 450–457.

Yamamura S, Morita Y, Hasan Q, Yokohama K, Tamiya E, Keratin degradation: a cooperative action of two enzymes from Stenotrophomonas sp, Biochemical and Biophysical Research Communications, 2002, **294**,1138-1143.

PREPARATION AND CHARACTERISTICS OF SURFACE MODIFIED PAN FIBER BY COLLAGEN PROTEIN

Ding Zhiwen*, Xiaoyan Pang , Xiqing Li

China Leather and Footwear Industry Research Institute, No.18 Jiangtai West Road, Beijing, China, 100015
E-mail: 13701315570@163.com
National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu China, 610065, E-mail: pang_xiaoyan@163.com
College of Resource and Environment, Shaanxi University of Science and Technology, Xi'an, China, 710021,
E-mail: 334080057@qq.com

PAN fiber for textile has similar mechanical properties to wool, such as good elasticity and intensity, but its moisture absorption and hand feeling are unsatisfied because its composition is different from wool. Collagen protein from leather has good moisture absorption and affinity to skin, the combination of collagen protein on PAN fiber surface can improve its properties difference from wool. In our research work, the cyano-group on PAN fiber surface is hydrolysed into carboxyl-group by NaOH, and acidylated into acyl chloride group, then reacted with collagen protein, to obtain surface modified PAN fiber. By this modifying method collagen protein is fixed on PAN fiber surface through covalent bond.

Infrared spectrum and SEM results show collagen protein has been combined on the surface of PAN fiber. Weight analysis shows the collagen protein content in the modified fiber is about 8%. The water absorption property of the modified fiber is 18.2%, which is improved by 93.6%. The moisture regain is 5.74%, which is improved by 280.1%. The specific resistance is reduced by 99.2%. The performance of PAN fiber is improved to a great degree after surface modified by collagen protein.

Keywords: Collagen protein, PAN fiber; Surface modification; Property anylysis

1. **INTRODUCTION**

PAN fiber has good elasticity and strength properties, and has the name of "synthetic wool", but its application is limited in decoration and knitwear due to its disadvantages of bad antistatic property and moisture regain property. Many chemical and physical modification methods are applied in the manufacture of PAN fiber to meet the customer's demands for comfortableness[1-2].

Collagen protein is isolated from animal skin and has the similar compositions to human skin, can be applied in many fields related to human life, such as cosmetic products, health care products and medical products. Collagen protein has good property of moisture absorption and affinity to skin, it can also be applied in the modification of synthetic fiber to improve its handle and moisture regain property[3]. There are several methods to modify PAN fiber with collagen protein, such as collagen protein co-polymerized with acrylonitrile monomer[4-5], or collagen protein mixed with polyacrylonitrile[6-7], to get collagen protein and polyacrylonitrile composite spinning solution and get collagen protein modified PAN fiber after spinning.

In this paper we take PAN fiber as raw material directly, and make collagen protein combine on the surface of the fiber, and give the fiber a collagen protein layer to improve its antistatic property and moisture regain property. This modifying method can avoid the destruction of fiber inner structure and improve the utilizing value of collagen protein which is on the fiber surface.

2. **MATERIAL AND METHODS**

The PAN fiber used in this work is 19mm∗1.5D short fiber purchased from Shanghai Kafa Special Fiber Co., LTD. Collagen protein was isolated from chrome shavings by alkali hydrolysis method. Sulfoxide chloride was purchased from Tianjin Fucheng Chemical Reagent Company. CBB(coomassie brilliant blue) G-250 was purchased from Shanghai Puzheng Biological Sci. & Tech. Co., LTD.

PAN fiber was dispersed in 12% NaOH solution and hydrolyzed at 80℃, then washed with deionized water to reach neutral and dried for further process application. Hydrolyzed PAN fiber (1g) was put into a three mouth flask, reacted with sulfoxide chloride at 80℃ for 30 minutes. Residual reactant was removed by reduced pressure distillation. 50 ml collagen protein solution was added into the flask and react with the acylated PAN fiber, and NaOH solution was added at the same time to adjust the pH value during the modifying reaction. The modified PAN fiber was washed by deionized water several times until the washing waste water show colorless, and then the fiber was dried and analyzed.

Collagen protein content of the modified PAN fiber was calculated as following:

$$\frac{W_2 - W_1}{W_2} \times 100\%$$

W_2: Weight of the fiber after modified with collagen protein
W_1: Weight of the PAN fiber as raw material before hydrolysis

Fiber was soaked in water for 1 hour, then remove the unbound water by centrifugation, the water absorption of the fiber was calculated as following:

$$\frac{W_4 - W_3}{W_3} \times 100\%$$

W_3: Weight of the dry fiber before soaking
W_4: Weight of the fiber after soaking and centrifugation

Fiber was put in the condition of temperature 20℃ and humidity 65% for 24 hours, then dried. the moisture regain property of the fiber was calculated as following:

$$\frac{W_6 - W_5}{W_5} \times 100\%$$

W_5: Weight of the dried fiber
W_6: Weight of the fiber after moisture absorption treatment

3. RESULTS AND DISCUSSION

3.1 The main factors affect the collagen protein content of the modified PAN fiber

$L_9(3^4)$ orthogonal experiment was carried out to study the main factors of the reaction between collagen protein and acylated PAN fiber in the modifying of PAN fiber. The factors include temperature, reaction time, amount of NaOH and amount of collagen protein. The factors and levels of the experiment is shown in table 1.

Table 1 Factors and levels of the reaction of collagen protein with acylated PAN aiber

Factors Levels	A Temperature(℃)	B 10%NaOH（ml）	C Time（min）	D Con. of protein（%）
1	40	0.5	5	2
2	60	1.0	10	5
3	100	1.5	30	7

Table 2 Results of orthogonal experiment of the reaction

Factors Experiments	A	B	C	D	Collagen protein content in the fiber（%）
1	1	1	1	1	1.77
2	1	2	2	2	2.83
3	1	3	3	3	1.49
4	2	1	2	3	5.17
5	2	2	3	1	4.88
6	2	3	1	2	3.01
7	3	1	3	2	1.61
8	3	2	1	3	2.05
9	3	3	2	1	1.07
K_1	6.09	8.55	6.83	7.45	
K_2	13.06	9.76	9.07	7.72	
K_3	4.73	5.57	7.98	8.71	
k_1	2.01	2.85	2.27	2.48	
k_2	4.35	3.25	3.02	2.57	
k_3	1.58	1.86	2.66	2.90	
R	2.77	1.39	0.75	0.33	

From the results of the orthogonal experiment, the order of the factors affects the collagen protein content in the modified PAN fiber is: reacting temperature, amount of NaOH, reacting time, concentration of collagen protein. The reacting temperature and the amount of NaOH are the most important factors to increase collagen protein content of the modified PAN fiber.

3.2 Influence of reacting temperature on the collagen protein content of the modified PAN fiber

The modifying reaction under different temperature was studied, and the amount of NaOH solution in the experiments is 0.8ml, 1.0ml, 1.2ml respectively. The reaction time in figure 1 is 5 minutes, and the reaction time in drawing 2 is 10 minutes.

From the results we can find high temperature is good for the reaction between collagen protein and acylated PAN fiber. But if the temperature is higher than 75℃, the collagen protein content in the fiber decreases with the temperature rising. This because acylated PAN can react with water at higher temperature, and the amount of collagen protein combined with PAN fiber is decreased accordingly. So the preferred reacting temperature is 75℃, under this temperature acylated PAN is easy to react with collagen protein and difficult to react with water.

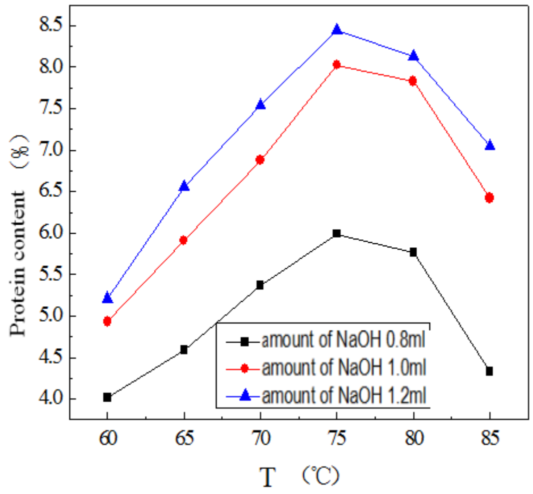


Figure 1：Reaction under different temperature（5min）

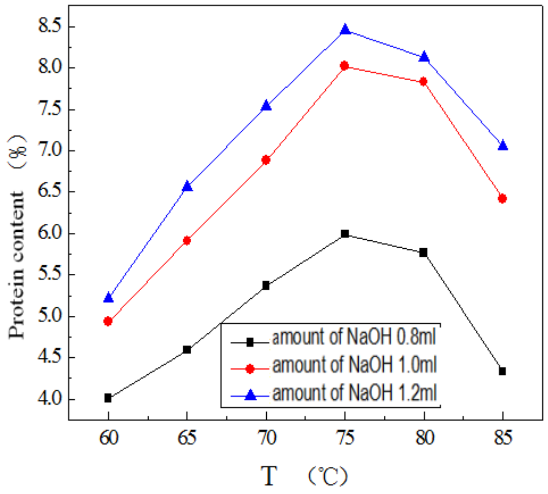


Figure 2：Reaction under different temperature（10min）

3.3 Influence of the amount of NaOH on the collagen protein content of the modified PAN fiber

Figure 3 shows the collagen protein content of the modified fiber prepared with different amount of NaOH under the condition of temperature 75℃, reacting time is 5, 10 and 30minutes respectively.

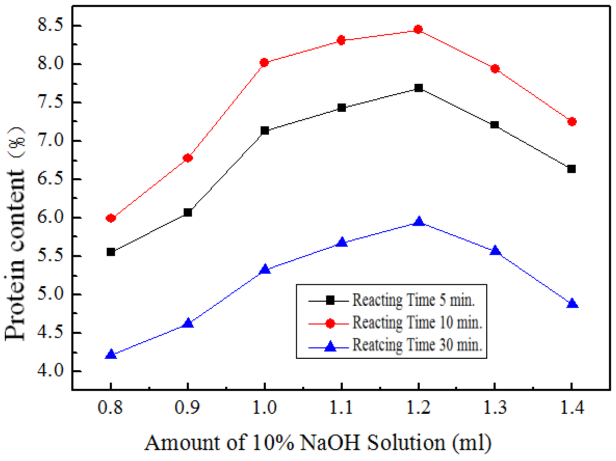


Figure 3 Influence of the amount of NaOH on the reaction

At the first the collagen protein content of the modified fiber goes up with the amount of NaOH solution increasing, this is because NaOH can neutralize the acid produced in the reaction and accelerate the reaction. When the amount of NaOH exceeds 1.2ml, the collagen protein content goes down with the amount of NaOH solution increasing, this is because if there is too much alkali in the system the acyl chloride group in acylated PAN fiber will react with water, and the amount of combined collagen protein in the fiber decreased. So the preferred amount of NaOH solution in the reaction is 1.2ml, the modified fiber with highest collagen protein content can be obtained.

3.4 Influence of reacting time on the collagen protein content of the modified PAN fiber

Figure 4 shows the collagen protein content of the modified fiber prepared at different reacting time under the condition of temperature 75℃, amount of NaOH solution 1.2ml. The reaction between collagen protein and acyl chloride group was very fast, it was finished within 10 minutes. The reacting time is 10 minutes preferably, and the collagen protein content of the fiber at this reacting time is 8.45%. The collagen protein content goes down with the reaction is prolonged further, because long reaction time make collagen protein hydrolyzed under alkaline condition.

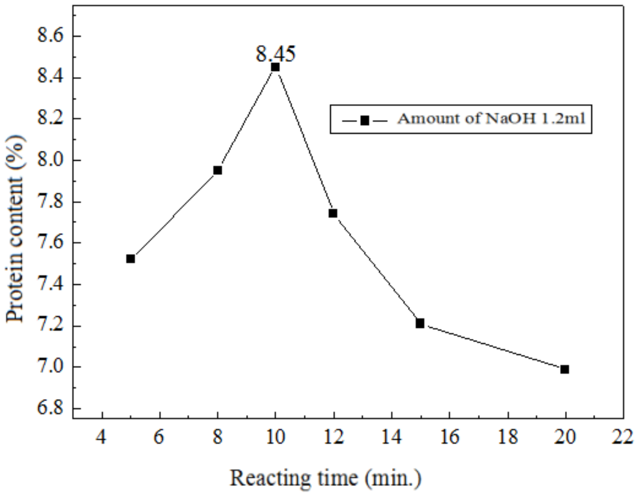


Figure 4 Influence of the reacting time on the reaction

3.5 FTIR-ATR analysis of the fiber

Comparing the infrared spectra of collagen protein modified PAN fiber with the original PAN fiber, there are new characteristic absorption peaks of protein amide bond 1669cm^{-1},1550cm^{-1} and hydroxyl group 3360cm^{-1} on the modified fiber spectrogram, at the same time the intensity of characteristic absorption peak of cyanogroup is decreased, indicating cyanogroup is hydrolyzed and collagen protein was fixed on the surface of PAN fiber.

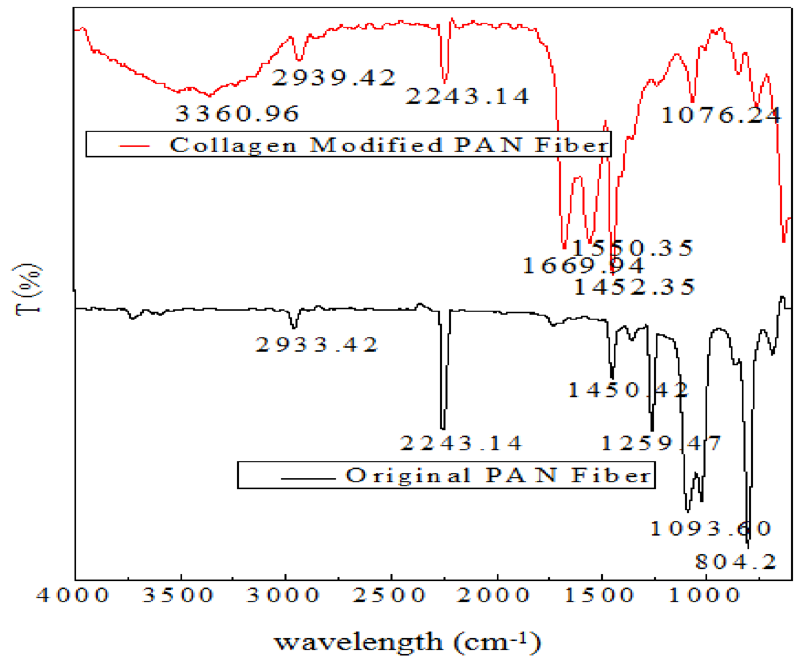


Figure 5 FTIR-ATR spectra comparison between modified PAN fiber and original PAN fiber

3.6 Amino acid analysis of the collagen protein modified PAN fiber

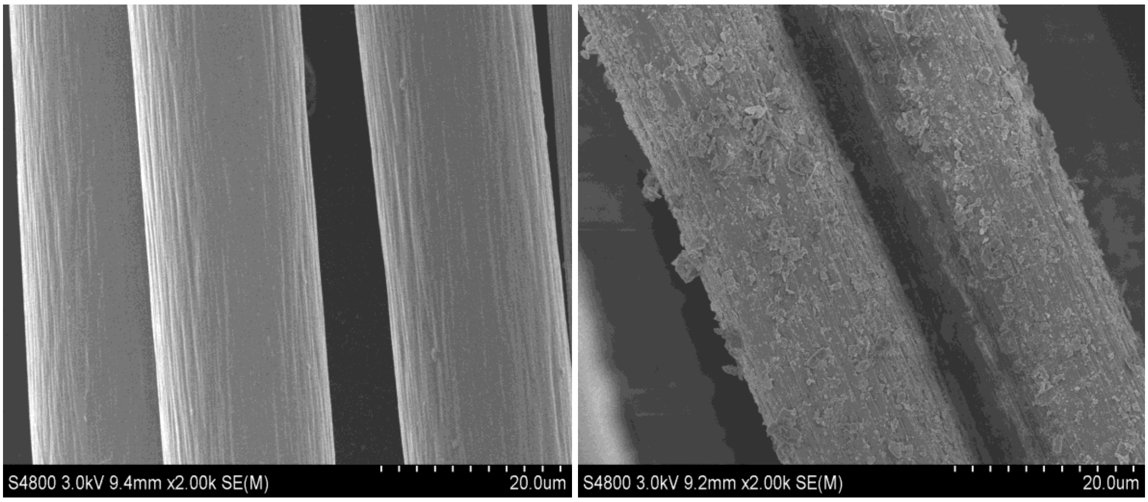
Table 3 Amino acid content analysis result of modified fiber

	Amino Acid	Retention Time（min）	Content（%）
1	Aspartic Acid (Asp)	10.547	0.220
2	Threonine(Thr)	11.912	0.035
3	Serine(Ser)	12.861	0.050
4	Glutamic Acid(Glu)	15.733	0.810
5	Glycine(Gly)	20.461	2.120
6	Alanine(Ala)	21.699	0.915
7	Cystine(Cys)	22.579	0.060
8	Valine(Val)	23.869	0.230
9	Methionine(Met)	25.741	0.075
10	Isoleucine(Ile)	28.243	0.160
11	Leucine(Leu)	29.293	0.320
12	Tyrosine(Tyr)	31.749	0.090
13	Phenylalanine(Phe)	33.805	0.030
14	Histidine(His)	38.021	0.080
15	Lysine(Lys)	41.227	0.280
16	Arginine(Arg)	45.749	0.420
17	Hydroxyproline(H-pro)	9.575	1.255
18	Proline(Pro)	16.733	0.920
Total			8.070

The analysis result shows the modified PAN fiber has 18 kinds of amino acid, which is similar to collagen protein. The total amino acid content of the modified fiber is 8.07%, it is lower than 8.45% which is measured by gravimetric method. This is because the amino acid combined with PAN can't be hydrolyzed totally and separated in the course of amino acid analysis. The amino acid analysis demonstrates that collagen protein is fixed on the PAN fiber.

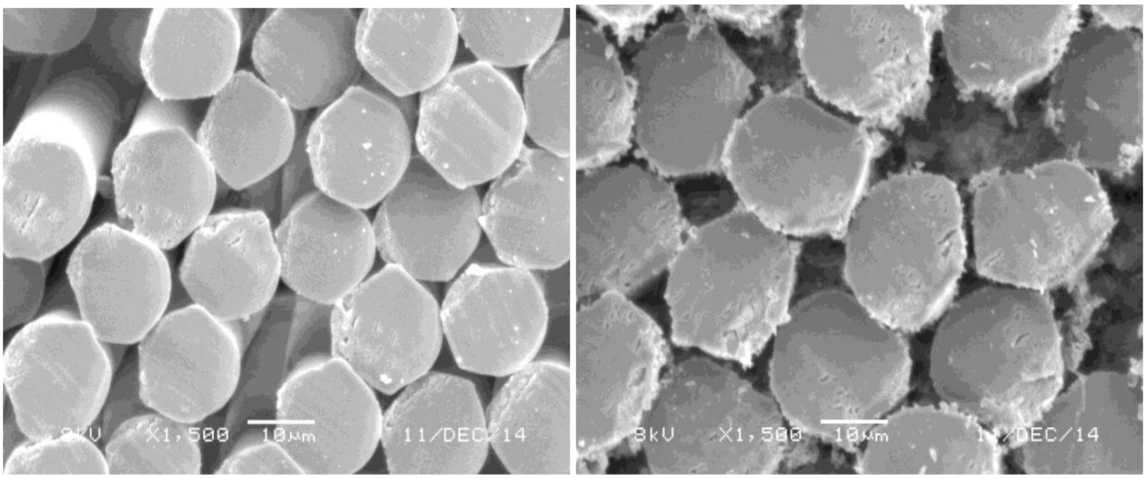
3.7 SEM images of the PAN fiber before modifying and the PAN fiber after modifying

Figure 6 and figure 7 show that after modifying the surface of the PAN fiber is covered a layer of collagen protein, and the inner structure of the PAN fiber is unchanged which is good to keep the strength of the fiber.



a) PAN fiber b) modified PAN fiber

Figure 6 SEM images of the outer surface of PAN fiber and modified PAN fiber



a) PAN fiber b) modified PAN fiber

Figure 7 SEM images of cross section of PAN fiber and modified PAN fiber

3.8 Mechanical properties of the modified PAN fiber

Table 4 shows the mechanical properties of PAN fiber and modified PAN fiber. After modifying the tensile strength of the fiber is increased by 43.0%, and the elongation of the fiber is decreased by 17.4%. The results indicate that the modifying reaction may form cross linking on the surface of the PAN fiber.

Table 4 Mechanical properties comparison of PAN fiber and modified PAN fiber

	PAN fiber	Modified PAN fiber	Increased percentage (%)
Tensile strength (cN/det)	3.72	4.32	43.0
Elongation (%)	24.22	20.01	- 17.4

3.9 Antistatic property of the modified fiber

Table 5 shows the resistivity of PAN fiber and the collagen protein modified PAN fiber. The specific resistance and volume specific resistance of the PAN fiber are all decreased by 99.2% after modifying. Low resistance is good for further processing of fiber, and suitable for clothing.

Table 5 Resistivity comparison of PAN fiber and modified PAN fiber

	PAN fiber	Modified PAN fiber	Decreased percentage (%)
Specific resistance （Ω·g/cm^2)	2.02×10^{10}	1.65×10^{8}	99.2
Volume specific resistance (Ω·g/cm^2)	6.5×10^{10}	5.3×10^{8}	99.2

3.10 Moisture regain property of the modified fiber

Moisture regain property is very important for clothing, it is related to comfortable wear of clothes. Pure PAN fiber has poor moisture regain property, it is only 1.51% from the result of table 6. Moisture regain of collagen protein modified PAN fiber can reach 5.74%, which is increased by 280.1%.

Table 6 Comparison of moisture regain between PAN fiber and modified PAN fiber

	PAN fiber	Modified PAN fiber	Increased percentage(%)
Moisture regain (%)	1.51	5.74	280.1

3.11 Water absorption property of the modified fiber

Collagen protein has good water absorption property, and the PAN fiber surface-modified by collagen protein has much better water absorption than pure PAN. Fig. 8 shows the water absorption of modified PAN fiber with different collagen protein content. Water absorption of the PAN fiber without modifying is 9.4%, water absorption of the PAN fiber with 4.88% collagen protein is 12.1% which is increased by 28.7%, water absorption of the PAN fiber with 8.45% collagen protein is 18.2% which is increased by 93.6%.

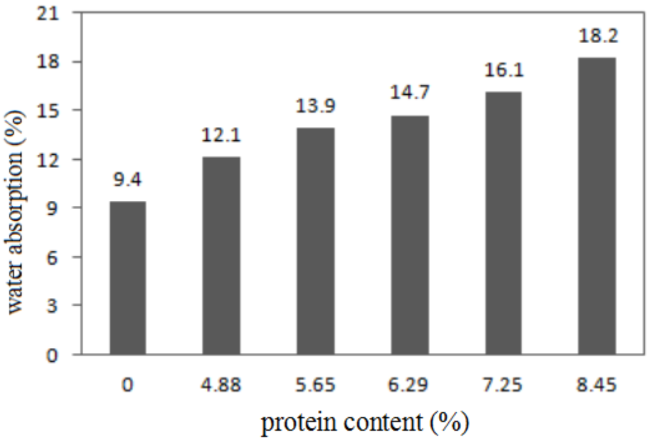


Fig.8 Water absorption of modified PAN fiber with different collagen protein content

4. CONCLUSION

The preferred conditions of the reaction between collagen and acylated PAN fiber is temperature 75℃, reacting time 10min, amount of 10%NaOH solution 1.2ml, collagen protein solution concentration 5%. The collagen protein content of the modified PAN fiber is 8.45%.

FTIR-ATR analysis, amino acid analysis and SEM images of the modified fiber demonstrate that collagen protein is combined on the surface of PAN fiber.

The water absorption property of the modified fiber is 18.2%, which is improved by 93.6% to PAN fiber. The moisture regain is 5.74%, which is improved by 280.1%. The specific resistance is reduced by 99.2%. The properties of PAN fiber is improved to a great degree after surface modified by collagen protein.

5. ACKNOWLEDGEMENTS

The authors are grateful to the National Natural Science Foundation of China (21376259) and National High Technology Research and Development Program (TS863) of China（2013AA065701）for financial support.

6. REFERENCES

[1] Zhu R T, Yan Y R, Zhan H Y, et al, Chemical Modification on Pan Fibers, J, Chemical Fiver & Textile Technology, 2007, 1, 16-20.

[2] Wang Q, Feng Y, Modification Technology for Polyacrylonitrile Fiber and its Application, J, Synthetic Fiber in China, 2010, (1), 7-10.

[3] Ma H F, Yao Y B, Research Process of Collagen Fiber Spinning, J, Shandong Textile Science & Technology, 2004, (4), 45-47.

[4] Wang Z X, Wang Y Z, Zhang W X, et al, Study on Copolymerization of Collagen/AN, J, Synthetic Fiber in China, 2007, (3), 18-20.

[5] Wang Y Z, Wang Z X, Zhang W X, et al, Solution Polymerization of Collagen and Acrylonitrile, J, Journal of Zhongyuan University of Technology, 2008, 19(2), 8-11.

[6] Ding Z W, Pang X Y, Liu N, Preparation of Polyacrylonitrile-collagen Composite Fiber Spinning Fluid, J, China Leather, 2013, 42(1), 14-18.

[7] Zhang Z H, Ma H F, Sun R J, et al, Structure and Performance of Collagen/PAN Composite Fiber, J, Polymer Materials Science and Engineering, 2009, 25(12), 69-72.

STUDY ON THE RECYCLING TECHNOLOGY OF UNHAIRING-LIMING AND TANNING WASTEWATER

Jin Li-qiang*, Zhang Zhuang-dou, Liu Jie, Zhang Fei-fei, Li Yan-chun, Qiang Xi-huai, Zhang Chuan-bo

BIOSK chemicals Co., Ltd, Shangqiu 476000, China, E-mail: support@biosk.cn
School of Leather Chemistry and Engineering, Qilu University of Technology, Jinan 250353, China E-mail: jin-liqiang@163.com
College of Light Chemical Science & Engineering, Shaanxi University of Science & Technology, Xian 710021, China E-mail: qiangxihuai@163.com

The recycling technology is one of the most important ways to realize the clean production in leather industry. In this study, a novel closed recycling technology of unhairing-liming and chrome tanning wastewater has been applied in mass production scale in a local tannery. In the recycling process, the content of various ions and TOC of the wastewater were measured. The collagen fiber dispersion and the distribution of ions in pelts were characterized. The shrinkage temperature and mechanical properties of leather obtained by the recycling technology were also tested.

All the trials showed that the novel closed recycling technology worked well without impairing the quality of the resultant leather and the zero emission of unhairing-liming and chrome tanning wastewater was realized. In the unhairing-liming step of the novel technology, the dosage of water, sulfide and lime were reduced by 80.8%, 33.3% and 23.4%, respectively. The collagen fiber bundles of limed pelts were split well. The distribution of calcium ion and sulfion in limed pelts was more uniform. 70% of salt and 20% of chrome tanning agent could be saved by recycling of chrome tanning wastewater. The shrinkage temperature of wet blue from different recycling times (from the first time to the 30 times) was all above 100^{o}C. With the increase of the recycling times, the grain surface color of the wet blue tended to be similar. Furthermore, the mechanical properties and yield of the leather in the recycling technology were improved.

Keywords: unhairing-liming wastewater; tanning wastewater; recycling technology; zero discharge; mass production

1. INTRODUCTION

The unhairing-liming and chrome tanning are two of the most important steps in the production process of leather making. The quality of unhairing-liming and tanning process will affect the following process as well as the properties of the finished leather. The traditional unhairing-liming wastewater contains large amount of sulfide, lime, protein and its degradation product. The tanning wastewater contains chrome complex and neutral salt. Therefore, the unhairing-liming and chrome tanning wastewater is the main source of pollution in leather manufacture. The terminal control method is usually used in the liming and chrome tanning wastewater treatment. But the treatment fee is high and the treatment system is not very effective.

The recovery and reuse of wastewater is one of the effective ways to realize the clean production of liming and chrome tanning (Thanikaivelan et al. 2005; Hu et al. 2011; Saravanabhavan et al. 2004; Rao et al. 2003), which has been paid more and more attention by researchers. In recent years, several patents have been granted to BIOSK chemical company about closed cycle technology of liming and chrome tanning effluent (Zhang et al. 2009; Zhang 2011; Zhang 2014).

According to the principle of this technology announced by BIOSK, the closed cycle technology of unhairing-liming and chrome tanning wastewater in production of cattle shoe leather was investigated. The aim of this research is to explore the technical points of the recycling technology of liming and tanning wastewater, and evaluate the effect of the process and the quality of the obtained products.

2. MATERIALS AND METHODS

2.1 Materials

The experiment chemicals were as following: Na_2S, NaHS (70%, flakes), lime and chrome powder were industrial grade. Degrease agent AN-C was supplied by LANXESS Inc. The liming auxiliary DO-pro and ELIPO, fungicide DK and basifying agent BE were supplied by BIOSK CO., Ltd. Lime dispersing auxiliary CR-2 was purchased from American BK Company. Especially for special illustration, the dosage of chemicals was calculated according to the weight of salting hide.

2.2 Liming wastewater recycling process

The traditional hair persevering process was shown in Tab. 1. The wastewater of experimental process was collected and then reused in the next production batch. Because of the restriction of experimental condition, only 80% of the liming wastewater was collected. The recycling route of the liming wastewater was shown in Fig. 1. A certain amount of sodium sulphide as well as the lime was supplemented in each recycling.

Tab.1 Conventional hair saving unhairing process

Process	Chemical	%	Temp. °C	Time
	Water	80	25	
Immunization stage	AN-C	0.1		
	DO-pro	0.8		
	NaHS	0.2		Run: 30 min
	Lime	1.2		Run: 20 min, standing: 20 min
Unhairing stage	NaHS	0.8		
	Na_2S	0.2		Run: 30 min
	Water	20	25	
Hair separation				Filtration with 30 min
Liming stage	DO-pro	0.4		
	Lime	1		

	Na_2S	1		Run: 30 min
				Run: 10min every half hour (4×)
	Lime	0.5		
	Water	50		
	CR-2	0.2		
	Lime	0.8		Run: 30 min
				Run: 5min every hour until next day

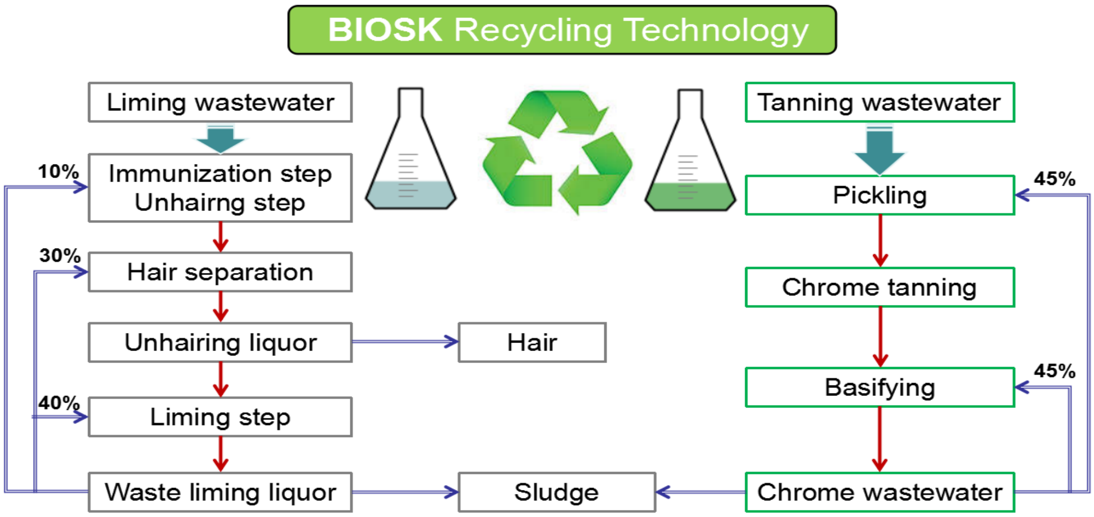


Fig.1 The recycling method of liming and chrome tanning wastewater

2.3 The recycling formulation of chrome tanning wastewater

The operating process of the chrome tanning wastewater was shown in Tab.2. The chrome-contained wastewater of experimental process was collected and then reused in the next production batch for pickling and tanning. Due to limitations of the experimental conditions, only 90% of chrome tanning effluent was collected. The recycling route of the chrome-containing wastewater was shown in the right side of Fig. 1.

Tab.2 The pickling and tanning process

Process	Chemical	Dosage %	Temp. (°C)	Time min)	Remark
Pickling	Salt	2-4	25		
	Chrome tanning effluent	100			
	Formic acid (85%)	0.5			1:10 diluting
	Sulfuric acid (96%)	1.7			1:10 diluting
	Pickling auxiliary D Mildew preventive DK	0.2 0.2		120	1:10 diluting pH: 2.0-2.5
Chrome tanning	Conducted in the pickling solution				
	Chrome tanning agent	5		180	
	Pickling auxiliary agent D	0.2	25		
	Basifying agent BE	0.2		120	pH: 3.2-3.4

	Chrome effluent (60°C)	100		240	Stay for overnight
					Run for 30min in the next day, pH:3.2-3.4

2.4 The chemical analysis of liming wastewater

The sample of liming wastewater was precipitated firstly. After natural sedimentation, 500 mL of the wastewater of different recycling technology was filtered by double layer gauze for two times. The filter liquor was taken to analysis.

2.4.1 The determination of Na_2S content

The content of sulfide in the wastewater was determined by filtration and iodimetry (Balasubramanian et al. 2000).

2.4.2 The determination of Ca content

2.4.2.1 The content of Ca in liming wastewater

The content of Ca was determined by EDTA complexometry method (Barrows et al. 1962).

2.4.2.2 The determination of Ca content in the pelt

The leather sample was ashed at 550°C firstly. Then the 1:1 hydrochloric acid was used to resolve the ash. Lastly, the sample was diluted. The titration process was similar to the determination of Ca in the wastewater.

2.4.3 The detection of Total Organic Carbon (TOC)

The TOC was detected by a TOC analyzer (TOC-L CPH CN20, SHIMADZU). The liming liquid waste was diluted 500 times and filtered through filter membrane (0.45 μm) before analysis.

2.4.4 The detection of buffer capacity

The buffer capacity of the liming liquid waste was detected by an automatic potentiometric titrator (ZDJ-4A, Rex Electric Chemical)..

2.5 Ts and analysis of chrome tanning wastewater

The TOC of chrome tanning wastewater was detected as mentioned above. The Ts of wet blue and the content of Cr_2O_3 in wastewater were also determined in accordance with Chinese standard QB/T 2713-2005 and GB 30486-2013.

2.6 The morphology and energy spectrum analysis of limed pelt

The limed pelt (1.5 cm×1.5 cm) was dehydrated for four times by 100 mL ethanol overnight and drying 24 h at 40°C. The grain and vertical section of the dried samples were analyzed by super depth of field microscope (ZEISS Smart zoom 5, Germany) and Environment Scanning Electron Microscope (ZEISS EVO18, Germany).

2.7 The physical and mechanical properties of the finished leather

The tensile strength, bursting strength, tear strength, contents of Cr_2O_3 and other related properties of the finished leather were tested according to Chinese industrial standard QB/T 2710-2005, 2712-2005, 2711-2005, 3812.15-1999, et al.

3. RESULTS AND DISCUSSION

3.1 Analysis of liming wastewater recycling technology

In our recycling experiment, the weight of leather was about 10 ton every time. The dosage of rawhide, sulfide, water, lime and waste lime solution in the recycling process were shown in Tab. 3. The dosage of water, sulphide and lime were reduced by 80.8%, 33.3% and 23.4%, respectively, as shown in Tab.4. In the whole process, the wastewater discharge was zero. Compared with the normal craft, the pelt obtained by this recycling technology was evenly swelled. The pelts also showed a clean surface and an obvious weight gain.

Tab.3 Information about the dosage of hides, chemicals and water in process

No.	The number of hides	Weight (kg)	Water (t.)	Recycled lime liquid (t.)	Sulphide (kg)	Lime (kg)
0	300	11126	15	0	245.8	389.4
1	243	9458	4	7.5	160.6	283.5
2	324	9370	1	11	149.8	280.7
3	317	11080	2	10	177	331.8
4	311	10586	2.5	12	168.5	307.8

Note: 0 represent the normal liming unhairing craft. “1” represents the first time recycling craft. “2” represents the second time recycling. “3” represents the third time recycling. “4” represents the fourth time recycling.

Tab.4 The saving materials in recycling process

No.	Water-saving rate (%)	Decrease in sulphide (%)	Decrease in lime (%)
1	65.2	34.7	27.2
2	91.7	39.1	27.9
3	83.3	28.0	17.4
4	82.8	31.4	21.0
Average	80.8	33.3	23.4

3.1.1 The Na_2S content analysis of liming wastewater

The Na_2S content of liming wastewater in different recycling time was shown in Fig. 2. The sulfide content of liming wastewater in normal process was higher than 5 g/L. The Na_2S content of wastewater in different time of recycling process was in the range of 4~6 g/L.

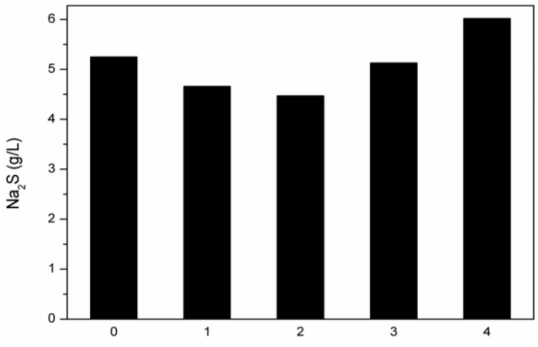


Fig.2 The Na$_2$S content of liming wastewater in different recycling time

3.1.2 The Ca content analysis of liming recycling wastewater

The variation of Ca content in different liming recycling wastewater was shown in Fig. 3(a). According to the results, the Ca content of wastewater in normal process was the highest. The content was about 2.25 g/L. In the following recycling technology, the Ca content in wastewater was in the range of 1.87~2.03 g/L. The rangeability is small. The variation of Ca content in different recycling process indicated that the recycling technology not only decreased the dosage of lime, but also decreased the residue content in the wastewater. The Ca content in the pelt was shown in Fig. 3(b). Compared with the conventional liming process, the Ca content of pelts in different recycling time decreased a little.

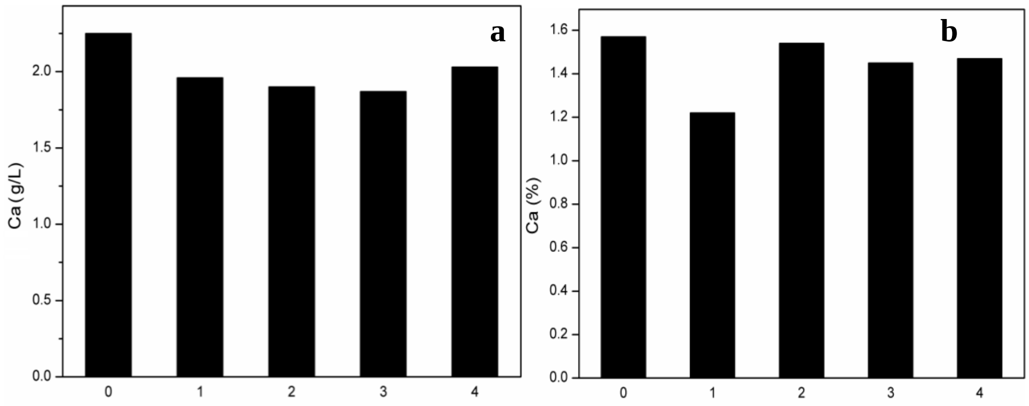


Fig.3 The content of Ca in liming waste liquor (a) and pelt (b)

3.1.3 The TOC analysis of liming wastewater

In order to analysis the content of organic material in the wastewater, the TOC was determined to characterize the pollution of organic material in the wastewater. The results were shown in Fig. 4. The TOC of wastewater from conventional method was 14750 mg/L. This was due to the dissolution of interfibrillar substance in liming process. In the liming process, the interfibrillar substance as well as part of collagen fiber would dissolve in the liming wastewater. Therefore, the content of organic material in waste water would increase. At the same time, the collagen fiber was dispersed sufficiently.

With the increase of recycling time, the TOC of wastewater increased due to the dissolution of organic material. After 4 times recycling, the TOC of waste water tended to be constant. Furthermore, the viscosity of liming wastewater did not tend to thicken. These might attribute to the hair persevering technology. In the hair filter process, part of the organic material would be absorbed into to the shedding hair and then filtered out the recycling system. So the recycling process could be carried out.

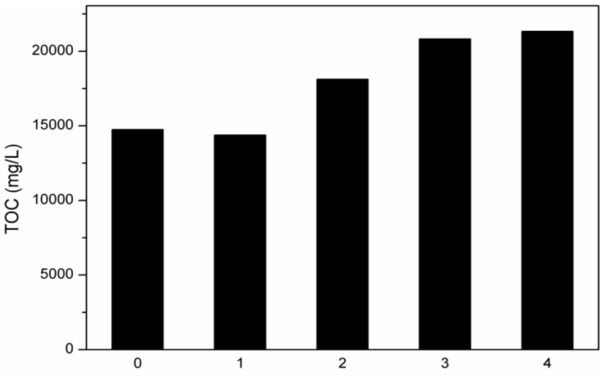


Fig.4 The TOC content of liming wastewater

3.1.4 The buffer ability of liming wastewater

The solubility of lime is limited, so the pH of saturated lime solution is in the range of 12~13. The mild liming condition makes the alkaline swelling slowly and uniformly. The operable and safety of lime swelling are attributed to the chemical property of lime. The potentiometric titration results of liming wastewater of different recycling time were shown in Fig. 5.

According to Fig. 5, the titration curves of $Ca(OH)_2$ solution had an obvious pH abrupt points. On contrary, no obvious abrupt point appeared in the titration curves of liming wastewater. So the liming wastewater displayed the outstanding buffering ability. This might be attributed to the existence of degradation products of interfibrillar substance in wastewater. Polysaccharose substance and protein showed a good buffering property, so the pH of the liming wastewater changed slowly when the acid was added. In the liming recycling system, the buffering properties of the liming wastewater would slow down the swelling rate of the raw hide. Furthermore, the occurrence of liming wrinkle in the liming pelt decreased. Then the obtained pelt became smoother and the yield of crust increased.

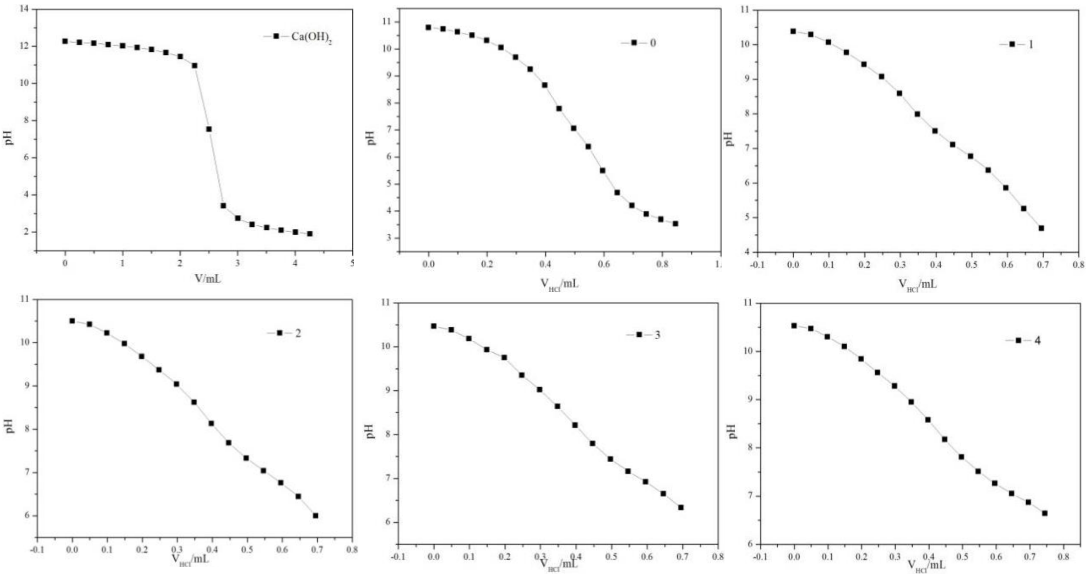


Fig.5 The potentiometric titration curve of liming wastewater at varied cycles

3.1.5 The fiber morphology of limed pelt

The morphology of grain of limed pelt was investigated by super depth of field microscope. The morphology of grain of limed pelt obtained by normal hair persevering process was shown in Fig. 6(a). The morphology of grain of limed pelt obtained by fourth times recycling process was shown in Fig. 6(b). The results indicated that the hair of two pelts was removed thoroughly. The hair pores were both clearly visible. This mean the hair root was also removed thoroughly. So the recycling technology of liming wastewater was safe and reliable. The SEM pictures of limed pelt from the original technology and the fourth times recycling process were shown in Fig. 7. According to Fig. 7, the dispersion of collagen fiber obtained by the fourth times recycling craft was similar with the normal craft.

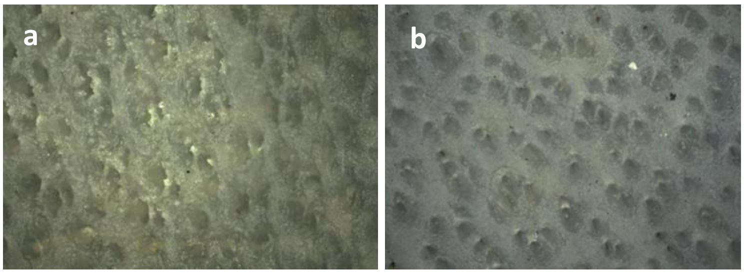


Fig.6 The grain of pelt from conventional process (a) and recycling process for 4 times (b)

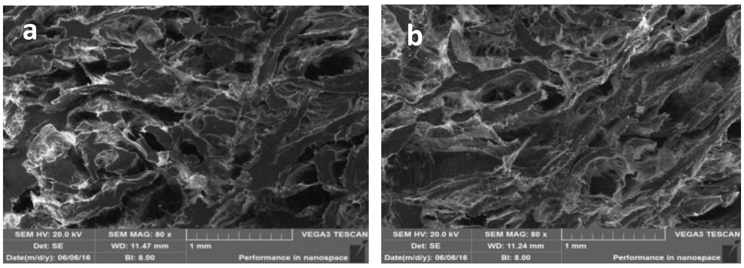


Fig.7 The SEM of cross section of pelt from conventional process (a) and recycling process for 4 times (b)

3.1.6 The distribution test of Ca and S and SEM analysis

The EDS spectrum of the leather sample obtained by the conventional technology was shown in Fig. 8(a). The EDS spectrum of the sample obtained by the fourth time recycling process was shown in Fig. 8(b). It indicated that the Ca content (red) of grain layer and flesh side was higher than that of the middle layer. After 4 times recycling, the distribution of Ca was uniformly distributed in the whole vertical section of limed pelt. This might attribute to the existence of large amount of organic material in the recycling liming wastewater. The swelling process was assuasive. The liming process was more uniform. As a result, the penetration of Ca was better. The S (blue) distribution in the samples from the conventional technology and the fourth time recycling process were similar. This might attributed to the solubility of sulfide. The penetration property of sulfide was higher than lime.

The distribution of Ca in the pelt obtained by the normal craft and the fourth time recycling craft were shown in Fig. 9. The Ca distribution in the pelt of the grain layer, middle layer and flesh side were 37.29%, 6.14% and 27.97%, respectively. Compared with the normal craft, the Ca distribution of pelt obtained by recycling craft in the grain layer, middle layer and flesh side were 29.33%, 12.95% and 23.91%, respectively. The results were in accordance with Fig. 8. The distribution of Ca in different layer was more uniformly.

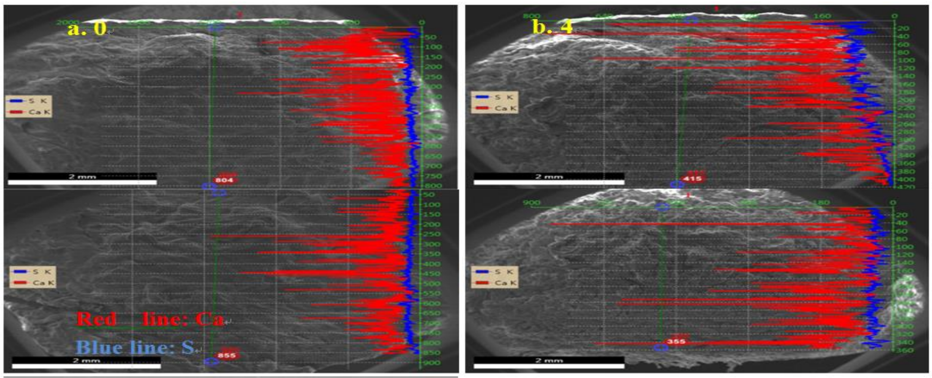


Fig.8 The EDX photo of cross section of pelt from conventional process (a) and recycling process for four times (b)

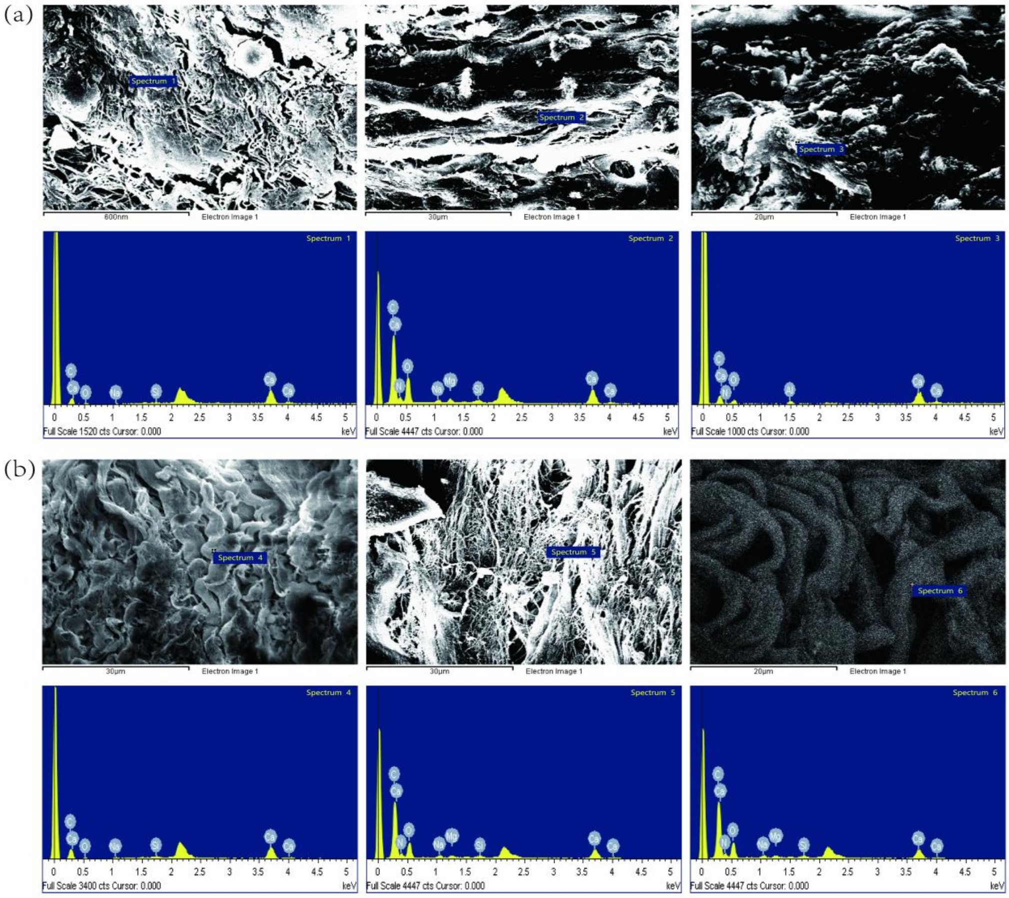


Fig.9 The distribution of Ca in the pelt obtained by the normal craft (a) and the fourth times recycling craft (b) (three layers form grain to flesh side of limed hide)

3.2 Chrome tanning wastewater recycling process

The Ts of wet blue obtained by different recycling time was determined. The experimental results were given in Tab. 5 and Fig. 10. According to Tab. 5, the Ts of wet blue didn't change so much with the increase of recycling time. The Ts of wet blue was in the range of 101~107^{o}C. The color of the grain surface of wet blue was consistent with the increase of recycling time as shown in Fig.10.

The variation rule of TOC and Cr_2O_3 content in the chrome tanning wastewater in different recycling time was shown in Tab. 6. According to Tab.6, the content of TOC and Cr_2O_3 in the recycling wastewater increased with the increase of the recycling time until the tenth time recycling. Then, the total organic compounds and remaining Cr component in the tanning wastewater reached equilibrium.

Tab.5 The variation of Ts of chromed leather with recycling times

Recycling time	0	1	2	5	10	15	25	30
Ts (^{o}C)	103.2	100.8	101.1	103.7	104.8	104.5	106.5	102.5

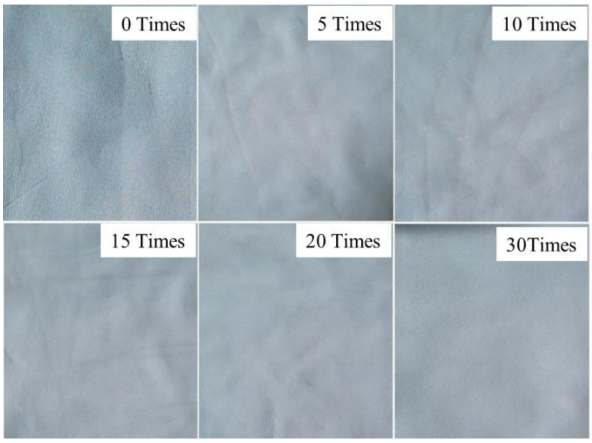


Fig.10 The relationship between the colour of chrome leather and recycling times

Tab. 6 The variation of the content of TOC and Cr_2O_3 with recycling times in chrome waste liquor

Recycling times	0	1	2	5	10	15	20	25	30
TOC(mg/L)	1750	1753	1767	2498	2823	2800	2872	2904	2787
Cr_2O_3 (g/L)	1.72	1.70	1.73	1.91	2.36	2.46	2.64	2.55	2.61

3.3 The physical mechanical properties test of finished leather

In order to assess the novel recycling technology, the physical mechanical properties of the finished leather samples obtained by conventional process and the recycling technology were compared. The results were shown in Tab. 7. The results indicated that the physical mechanical properties of finished leather were not influenced by the recycling technology. On the contrary, the tensile strength and tear strength of leather sample from the recycling technology were better than that of the sample obtained by the conventional technology. Furthermore, the yield of leather in the recycling technology was 95%, while the conventional technology is about 93%. This might attribute to the uniform swelling process of the collagen fiber in the recycling of liming wastewater, and the loss of the collagen content was less.

Tab.7 The physical and mechanical tests of the resultant leather

Samples No.	Tensile strength Crosswise (N/mm^2)	Tear strength Crosswise (N/mm)	Bursting strength (N/mm)	Cr_2O_3 (%)	Yield of leather (%)
0	10.58	54.35	22.38	4.82	93
4	10.86	59.60	21.83	4.98	95

4. CONCLUSION

A novel closed recycling of wastewater technology was applied and the zero discharge of liming and chrome tanning wastewater was realized. Compared with the normal process, the novel recycling technology could save more than 80.8% water, 33.3% of sulfide and 23.4% lime in liming process.

While in the chrome tanning wastewater recycling craft, 20% of the chrome tanning agent as well as 70% of salt were saved.

In the liming wastewater recycling process, the reduction of the dosage of lime and sulfide didn’t affect the removing efficiency of hair. The distribution of lime in the limed pelt was more uniform. In the chrome tanning recycling process, the special auxiliary can prevent the deterioration of the chrome tanning wastewater.

The physical and mechanical properties of the leather sample obtained by recycling craft were similar with the sample obtained by the normal craft. Furthermore, the yield and the chrome content in the leather sample obtained by recycling craft are higher than the leather sample obtained by the conventional process.

5. ACKNOWLEDGEMENTS

We acknowledged the Xinghao company to supply the pilot plant test space. We also acknowledged the contribution made by the researchers of Qilu university of technology to analysis the wastewater content as well as the physical and chemical test of the finished leather.

6. REFERENCE

1. Thanikaivelan P, Rao J R, Nair B U, et al. Recent trends in leather making: processes, problems, and pathways[J]. Critical Reviews in Environmental Science and Technology, 2005, 35(1): 37-79.
2. Hu J, Xiao Z, Zhou R, et al. Ecological utilization of leather tannery waste with circular economy model[J]. Journal of Cleaner Production, 2011, 19(2): 221-228.
3. Saravanabhavan S, Thanikaivelan P, Rao J R, et al. Natural leathers from natural materials: progressing toward a new arena in leather processing[J]. Environmental science & technology, 2004, 38(3): 871-879.
4. Rao J R, Chandrababu N K, Muralidharan C, et al. Recouping the wastewater: a way forward for cleaner leather processing[J]. Journal of Cleaner Production, 2003, 11(5): 591-599.
5. Zhang Z D, Yang Y L, Xu F, et al. Recycling of wastewater from raw hide to wet blues in leather manufacture[C]. XXX Congress of the International Union of Leather Technologists & Chemists Societies, Proceedings. 2009: 119-128.
6. Zhang Z D. Leather production process for recycling waste water from soaking to dyeing[P]. CN10253405, 2011-01-05.
7. Zhang Z D. Circular project for realizing near zero discharge of tanning waste water[P]. CN:104843807, 2014-02-15.
8. Balasubramanian S, Pugalenthi V. A comparative study of the determination of sulphide in tannery waste water by ion selective electrode (ISE) and iodimetry[J]. Water Research, 2000, 34(17): 4201-4206.
9. Barrows H L, Simpson E C. An EDTA method for the direct routine determination of calcium and magnesium in soils and plant tissue[J]. Soil Science Society of America Journal, 1962, 26(5): 443-445.

DIFFERENT PRE-TREATMENTS OF CHROME TANNED LEATHER WASTE AND THEIR USE IN THE BIOGAS PRODUCTION

Carolina Gomes*, **Michael Meyer**, **Jens-Uwe Repke**

Forschungsinstitut für Leder und Kunststoffbahnen (FILK) gGmbH, Meißner Ring 1-5, 09599 Freiberg, Germany, Email: carolina.scaraffunigomes@filkfreiberg.de
Dynamik & Betrieb techn. Anlagen, TU Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

Leather industry has undeniable economic and environmental importance converting by-products of the meat industry in value-added products. However, leather production generates huge amount of solid wastes. Usually, tanning process is done with chromium salts. Consequently a substantial part of the wastes are chromium tanned leather shavings (CTLW), which are mostly disposed of through landfill or incinerated. CTLW are collagen residues produced in tanneries which are very stable towards temperature and enzymatic degradation thanks to natural cross-links in the collagen structure and chemical cross-links between collagen fibers formed in the tanning step. As collagen is organic matter it can be considered for biogas production through anaerobic digestion but to ease enzymatic degradation and produce biogas a previous denaturation of the structure has to be carried out.

The goal of this study is to accelerate and improve biogas production when using CTLW. Autoclaving, extrusion, and hydrothermal treatment were performed as pre-treatments of the wastes. The pre-treated samples were analyzed regarding their degradation degree. Results showed that the pre-treatments accomplish to degrade the structure. Those that underwent autoclave treatment (120 °C) show more than 90% enzymatic degradation after 192 minutes of pre-treatment. Results for the extruded samples vary with operation conditions, and it was possible to reach 35% of degradation at 170 °C. The hydrothermally treated sample at 170 °C reached 90% of degradation. The untreated CTLW was only 6% degraded. During biogas production pre-treated samples were able to start production approximately five days before the untreated sample and presented higher biogas yield.

Keywords: Leather wastes, Biogas, Collagen

1. INTRODUCTION

1.1. Chromium tanned leather wastes and their disposal

In 2014, the manufacture of leather and related products in the European Union generated EUR 54 billion in turnover and employed 447.535 people (GROW 2016) highlighting the importance of the leather industry in this region. This industry also has an important environmental role, since its main raw material (hides) is a by-product of the meat industry.

Europe alone is responsible for the largest part of the global leather production, around 25%, generating about 170,000 ton of tanned leather wastes annually (Dahalayan et al. 2007). As the chromium-based tanning process is predominantly followed worldwide (Agrawal et al. 2006) most of these wastes will contain Cr^{3+} and need special handling. Currently, in most cases the chromium tanned leather wastes are disposed of through landfill or incineration processes, despite the ecological consequences (Pati et al. 2014). In disposal sites the leaching of Cr^{3+} from wastes can pollute groundwater. The incineration at elevated pH (9-10), in the presence of an excess of oxygen, can lead to conversion of Cr^{3+} to Cr^{6+}, which is a well known carcinogen (IULTCS 2008; Kolomaznik et al. 2008).

Increased environmental restrictions and escalating landfill costs have encouraged the leather industry to develop cleaner technology by minimizing wastes generated and maximizing those reused (Mu et al. 2003). Attempts have been made to replace the chromium in the tanning process but the obtained results cannot reach the quality of the chromium tanned leather. An option would be using vegetable agents in the tannery process, but those tanning agents cannot be considered more environmentally friendly than chrome tanning, due to the high waste water load and low treatability in conventional systems (IULTCS 2008). Therefore, the leather industry continues to face the handling and disposal problems of CTLW.

1.2. Alternative management of CTLW

Among the methods of reutilization of CTLW the biogas production through its anaerobic digestion stands out due to its ability to reduce the final amount of wastes and generate renewable energy simultaneously, low level of process complexity and low cost. Until present few studies about this subject have been published. They demonstrate that it is possible to produce biogas from CTLW but, due to very long times needed for the digestion, this method must be further developed to reach industrial feasibility.

The process is nothing more than anaerobic digestion of organic matter, a quite complex microbial process that takes place in the absence of oxygen with many types of strictly and facultative anaerobic bacteria (Murphy and Thamsiriroj 2013; Deublein and Steinhauser 2008). Biogas is the final product, which is a mixture of methane (55-70%) and carbon dioxide (30-45%) with traces of other gases (Deublein and Steinhauser, 2008). Mata-Alvarez et al. (2014) examined the papers about anaerobic digestion published between 2010 and 2013 and concluded that the most frequent main substrates studied are animal manures (54%), sewage sludge (22%) and the organic fraction of municipal solid waste (11%). At the same time, the most used co-substrates are industrial waste (41%), agricultural waste (23%) and municipal waste (20%).

As CTLW are considered complex wastes due their high chromium content, most of the biogas production papers analyzing the digestion of tannery wastes focus their efforts in the digestion of fleshings (Shanmugam and Horan 2009), sludge from the wastewater treatment (Kameswari et al. 2014a), wastewater (Banu and Kaliappan 2007), or the co-digestion of two of them (Zupancic and Jemec 2009; Thangamani et al. 2010 and 2015; Kameswari et al. 2011; 2012; 2014b and 2015; Ravindranath et al. 2015).

Tanned leather wastes are composed of organic matter, hence they can be used as raw material to produce biogas, even though leather itself is slowly biodegradable. The treatment to which hides undergo to produce leather with different chemicals (tanning process) makes them even more stable. This approach would become more feasible if a simple method to reverse the effects of tanning could be developed (Covington 2009).

More recently the investigation of CTLW's anaerobic digestion has started. Dhayalan et al. (2007) and Ferreira et al. (2010) studied the anaerobic digestion of CTLW. The former concluded that the degradation of this waste is possible using anaerobic sludge and it is better than vegetable tanned leather waste and the latter that the results are dependent on the anaerobic sludge concentration. Agustini et al. (2015) also studied the degradation of CTLW and detected 45% of methane in the produced biogas. In all cases, the experiments lasted one to four months, a time considered too long for industrial purposes.

Due to these difficulties there are currently no biogas plants in the industry using CTLW as main substrate. However, the tannery SÜDLEDER (Rehau, Germany) already has a biogas plant in operation using their own tanning wastes (hair, protein, fat, and waste water) to produce energy (Schuberth-Roth 2013). This kind of initiative illustrates the interest of the industry in biogas production, nevertheless the use of a substrate as complex as CTLW needs to be further developed.

Chrome tanned leather is a collagen fibrous material. Hence to understand leather it is important to begin by understanding the structure of collagen, which is among the most common fibrous proteins and it is present in tendons, ligaments, bones, dentin, skin, arteries, cartilage, and in most of the extracellular matrix in general (Fratzl 2008).

1.3. Collagen structure

At present over 50 collagens and collagen-like proteins are known, type I collagen being the most common protein in mammals (Hulmes 2008). These molecules are assembled in different fibrous structures with quite different properties, such as elastic skin, soft cartilage, and stiff bone and tendon (Fratzl 2008). What all the collagen molecules have in common is that they are composed of three polypeptide chains forming a triple helix arrangement. Each of the chains contains one or more regions characterized by the repeating amino acid motif (Gly-X-Y), where X and Y can be any amino acid (Hulmes 2008).

Several collagen molecules are stabilized by the development of molecular cross-links between them forming the fibrils and, subsequently, different kinds of tissues (Wess 2008). The resulting high mechanical strength and resistance to heat and bacterial degradation of collagen fibers motivated their use in the leather industry. Despite the natural collagen features there is a need to further stabilize collagen fibers by chemical cross-linking increasing their mechanical strength, their denaturation temperature, and susceptibility to enzymatic degradation (Avery and Bailey 2008). This chemical cross-linking process applied to hides is known as the leather manufacturing process.

As mentioned above, collagen molecules are not susceptible to degradation by enzymes because of their stable structure, and the tanning process increases this stability. The anaerobic digestion is based on this kind of degradation; hence this characteristic would preclude the digestion. To enable the process it is necessary to perform a prior degradation of the structure, which is normally accomplished increasing the temperature up to the denaturation temperature. Denaturation of collagen happens when this material is exposed to the denaturation temperature or higher. In this process the collagen structure collapses into gelatin chains (Avery and Bailey 2008). The random structure of gelatin loses the former high stability and can be easily degraded. However, CTLW has a denaturation temperature between 110 °C and 120 °C, which requires a denaturation process at these temperatures. After such treatment the chrome tanned collagen is as degradable as the raw collagen, and the denatured collagen behaves just like any other protein, but containing some inert Cr^{3+} (Covington 2009).

1.4. Objectives

The aim of this study is to accelerate and improve the biogas production process through anaerobic digestion of chromium tanned leather shavings (CTLW) enabling its application in the industry. For this purpose, CTLW underwent pre-treatment with different heating and mechanical technologies. The modifications caused in the collagen structure of this waste were evaluated with different methods, and some of the pre-treated samples were tested for biogas production.

2. MATERIAL AND METHODS

This study was developed in three different steps. At first, CTLW underwent pre-treatment to initiate material degradation. Thereafter, the pre-treated samples were assessed regarding their degree of degradation with different methods. Finally, the biogas building potential of some selected samples was investigated through biogas production trials in order to prove the feasibility of this method.

2.1. Material

Chromium tanned leather shavings (CTLW) samples from the shaving operation of the leather-making process were obtained from a local tannery and characterized regarding their volatile matter (DIN EN ISO 4684:2005 – Leather – Chemical tests – Determination of volatile matter), ashes (DIN EN ISO 4047:1998 Leather - Determination of sulphated total ash and sulphated water-insoluble ash), and chromic oxide content (DIN EN ISO 5398-1:2007 - Leather - Chemical determination of chromic oxide content). The results for the CTLW characterization are shown in Table 1.

Table 1: Leather shavings characterizations.

CTLW	
Volatile Matter (%)	20.9 ± 0.18
Ashes (%)*	11.0 ± 0.01
Chromium (%)*	4.4 ± 0.05

*Dry basis; mean ± standard deviation, n = 3

2.2. Pre-treatments

In order to denature the CTLW and favor the waste degradation and biogas production different heat and mechanical pre-treatment techniques were tested.

2.2.1. Autoclave

In order to reproduce the autoclaving conditions (high temperature and pressure) the trials were carried out using screw cap micro tubes tightly closed through O-ring sealing and a block heater (Stuart SBH130D) at 120 °C.

The CTLW were prior moistened with distilled water until saturation and left overnight at room temperature. This procedure is carried out in order to favor collagen denaturation, the main aim of this pre-treatment. All the samples were placed in the micro tubes, tightly closed, and subsequently placed in the block heater at 120 °C. The micro tubes were preheated for 3 minutes and 30 seconds, the estimated time necessary for the samples to reach the autoclaving temperature. Each sample was exposed to the autoclaving conditions for a predetermined time (3 to 384 minutes). Thereafter the samples were dried in a drying oven at 30 °C for one day.

2.2.2. Extrusion

Extrusion was performed with a co-rotating twin-screw-extruder Werner & Pfleiderer ZSK 25 at different temperatures (100 °C, 130 °C, 150 °C, and 170 °C) and humidity conditions (dry or wet) in a continuous process. The wet CTLW were prior moistened with water, well homogenized and left overnight. The dry samples were handled without any humidification process, exactly as delivered from the tannery. This process starts by feeding CTLW from a hopper into the barrel of the extruder. Subsequently the material is gradually degraded by mechanical energy generated by turning screws and by heaters arranged along the barrel, taking approximately 3 minutes.

Samples originated from dry and wet CTLW differ in appearance. The extrusion of dry CTLW resulted in samples with granular appearance, on the other hand the wet CTLW gave rise to a powder sample.

2.2.3. Hydrothermal treatment

CTLW were subjected to hydrothermal treatment through a continuous autoclave system attached to a refiner (ANDRITZ) at different temperature and pressure conditions. The temperature was adjusted regarding the saturated steam relative pressure. However, due to technical reasons the temperature was not as exact as expected (140 °C, 150 °C, and 170 °C). The pre-treatment time was approximately 45 seconds.

2.3. Assessment of the pre-treated samples

The susceptibility to anaerobic degradation of the pre-treated samples and the leather shavings were evaluated with two methods. The enthalpy measured with the DSC (differential scanning calorimetry) method represents the enthalpy of the denaturation process. In other words, the necessary energy to break down the hydrogen bonds that stabilize the triple helix. The degradation by trypsin breaks down covalent bonds between carbon atoms, a process similar to the actual enzymatic digestion.

2.3.1. DSC

Thermal profiles of the pre-treated samples were taken from 0 to 130 °C using DSC (DSC 1 STAR^{e} System Mettler Toledo) to assess thermal changes as a function of input temperature. pH was previously adjusted to 7 washing the samples with a KH_2PO_4/K_2HPO_4 buffer solution.

2.3.2. Degradation by trypsin

The denaturation degree of the pre-treated samples was measured with the aid of trypsin, an enzyme that acts to degrade protein. This enzyme test is based on the measurement of the degradation speed of heat treated leather. As the not denatured collagen is stable against enzyme degradation it is possible to determine the fraction of the samples which was denatured in the pre-treatment. The samples are placed in safe-lock microcentrifuge tubes with buffer solution and left overnight. Then the trypsin solution (1382 U/mL) was added at 37 °C (block heater Stuart SBH130D) during 5 hours. The degradation degree by trypsin at certain time (DD_t) is the portion of the sample that solubilizes in water after treatment with trypsin and it is represented by Equation 1:

$$DD_t = 100 - \left(\frac{w_f}{w_0} . 100\right) \% \qquad \text{Eq. (1)}$$

Where w_0 (mg) is the onset weight of the CTLW samples and w_f (mg) is the weight after the predefined treatment time, both weights were considered on a dry basis.

2.4. Biogas Production

Anaerobic digestion experiments were performed under mesophilic conditions (37 °C ± 2 °C) according to VDI 4630 (2006) in triplicate. The tests were conducted using 65 ml reactor flasks in two batches, with agitation (shaking water bath julabo SW-20C at 150 rpm) and without agitation (drying unit Fratelli Carlessi ARMADIO 5B). The gas production was monitored on a daily basis with a digital manometer (Leo 3 Keller). The mesophilic anaerobic inoculum was anaerobic sludge from the local sewage treatment plant. Biogas production is given in norm liters (273 K and 1013 hPa) per kg of organic dry matter (l_N.kgo_{DM}).

At the end of the process the resulting biomass was analyzed regarding its pH, volatile matter (DIN EN ISO 4684:2005), ashes (DIN EN ISO 4047:1998), and chromic oxide content (DIN EN ISO 5398-1:2007). The results were useful to develop the mass balance necessary to understand the ongoing processes in the biogas production and the actual final degradation of the substrates.

3. RESULTS AND DISCUSSION

3.1. Assessment of the pre-treated samples

Based on analysis of DSC and degradation by trypsin results (Figure 1) it is possible to conclude that the pre-treatments accomplished to degrade the triple helical structure of the samples. In all cases the degradation by trypsin is more sensitive to evaluate the susceptibility of the pre-treated samples to enzymatic degradation than DSC. The good results presented by the pre-treated samples even with more than 4% chromium content indicate that chromium in this quantity is not toxic for trypsin, which implies that the waste will probably not be toxic for the enzymes in the anaerobic digestion.

The autoclaved samples (Figure 1.a) even with short pre-treatment times presented high degradation. After only three minutes of thermical pre-treatment the degradation of the wastes went from 6.7% to 25.8% and within only 24 minutes it was possible to have more than 50% of degradation reaching more than 90% after 192 minutes. After 192 minutes of heat treatment the degradation reaches a plateau and any longer autoclaving process would not be worthwhile.

Figure 1.b shows that with extrusion it is possible to increase the degradation degree by trypsin of the untreated sample from 6.7% up to 35.2% at the highest tested temperature. Results showed an increasing tendency of degradation with increasing extrusion temperature. The previously

moistened extruded samples obtained slightly higher degradation levels. Nevertheless, it is still preferable to perform the process of humidification of the samples before the extrusion due to the ease of handling with granular samples instead of powder.

The a) othermally treated samples showed a linear growth trend with the temperature. The sample pre-treated at 170 °C reached a degradation by trypsin of 90% (Figure 1.c). The samples also differed in appearance. The sample pre-treated at 170 °C, which reached the highest degradation degree, had its collagen structure affected by the high temperature turning completely into gelatin. Samples pre-treated at 150 °C and 140 °C are very similar, with a doughy appearance.

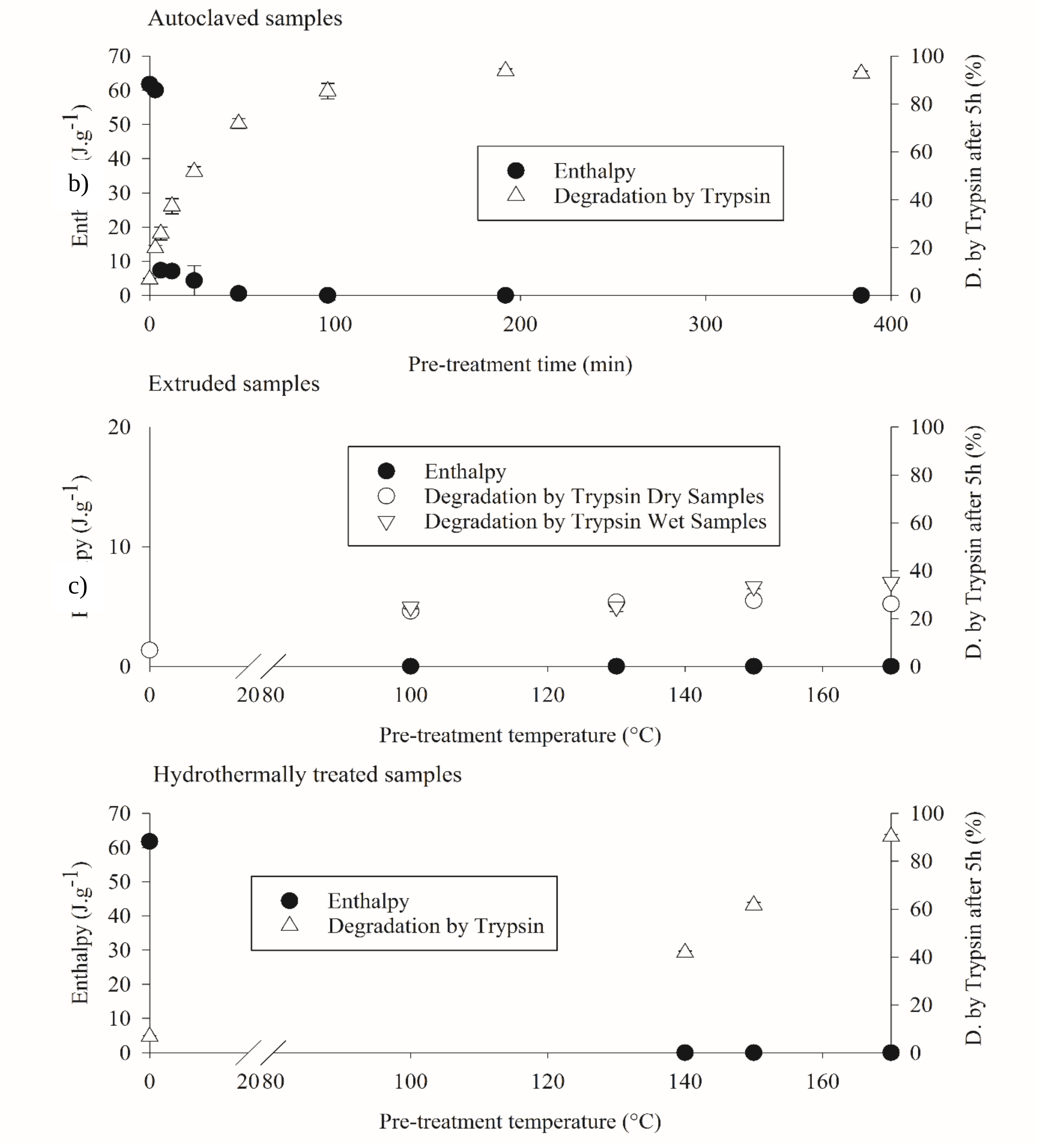


Figure 1: Enthalpy of the denaturation process and degradation degree by trypsin of CTLW and autoclaved samples as a function of the pre-treatment time (a), extruded samples (b), and hydrothermally treated samples as a function of the pre-treatment temperature (c).

3.2. Biogas Production

Two of the extruded samples and the untreated leather shavings were tested for biogas production. The sample extruded dry at 100 °C (E100D) and extruded wet at 170 °C (E170W) were selected as they represent the extremes of the extrusion treatment, being E100D the sample with the lowest degree of treatment and E170W the highest degree of treatment. Results are represented in Figure 2.

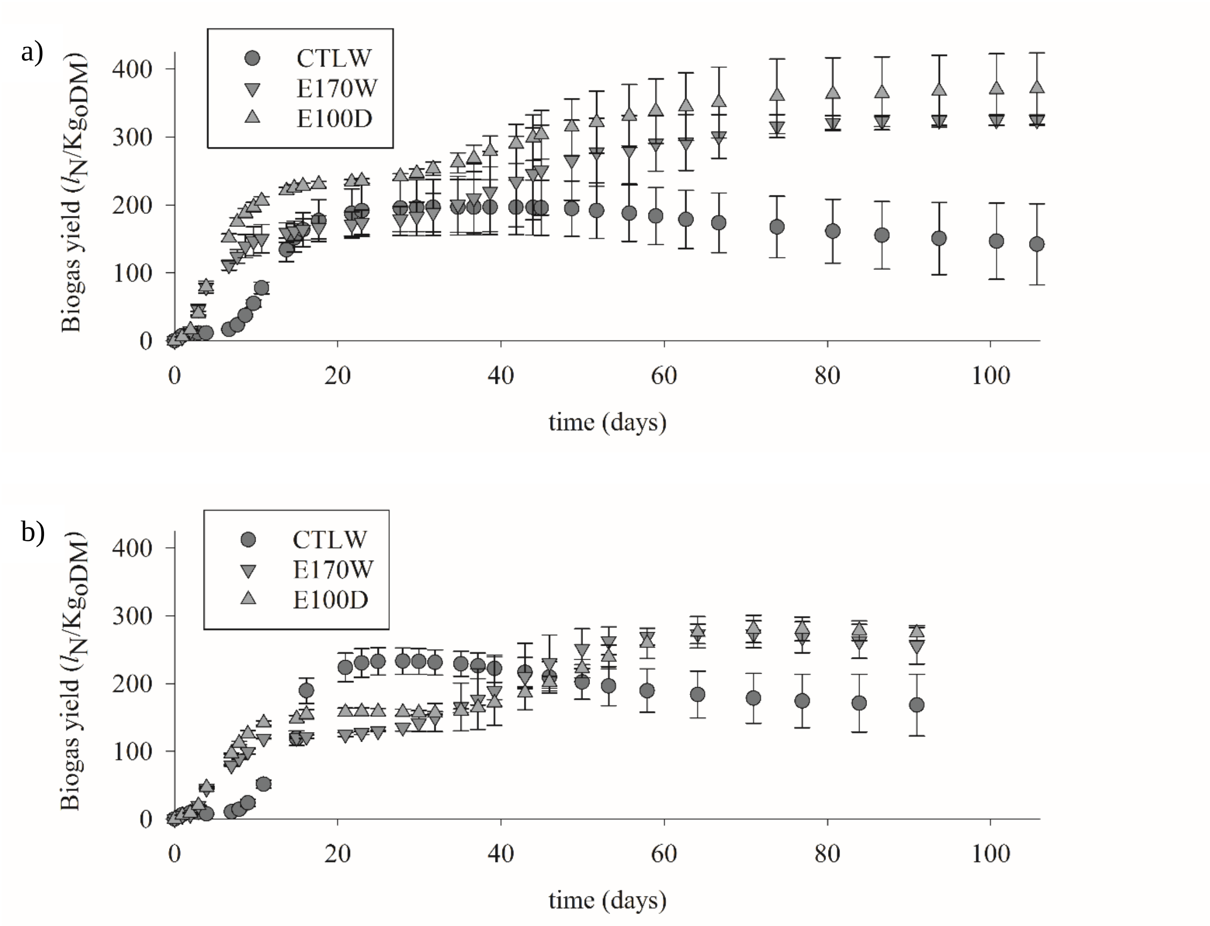


Figure 2: Cumulative biogas production for CTLW, E170W and E100D in agitated bioreactors (a) and in non-agitated bioreactors (b).

Comparing the untreated and the extruded samples for biogas production, the pre-treated samples were able to start production approximately five days before the untreated sample. Moreover after a lag-phase the extruded samples start to produce again, and diauxia (two phase decomposition) was observed, while the leather shavings remain stagnated. Diauxic growth is commonly seen in aerobic systems but not much information is available for anaerobic systems. Marin et al. (2010) reported diauxic growth curves for substrates containing protein and its occurrence was attributed to the presence of easily accessible biodegradable compounds that are digested first. The shape for the CTLW curve indicates a retarded degradation, what happens when the substrate degrades with difficulty (VDI 4630 2006).

In comparison with the untreated sample, the extruded samples presented higher final biogas yields in both cases indicating that the pre-treatment is able to ease the process. When comparing the extruded samples it is possible to see that they presented very similar results, which happened in the agitated and non-agitated reactors, although E100D was less degraded by trypsin E170W. A reason can be, that this sample is a powder like material favoring the mass transfer inside the reactors and hence its contact with the inoculum and anaerobic bacteria.

A comparision of the results for both batches (with and without agitation) indicated that agitation favors the biogas production. The E170W sample had final biogas yields of 325.0 ± 7.6 and 273.4 ± 14.5 $l_N.kgo_{DM}$ in the trials with and without agitation respectively. The E100D sample had final biogas yields of 371.2 ± 52.7 and 280.8 ± 20.1 $l_N.kgo_D$, an increase of more than 30% for the trials with agitation. For the untreated sample the final yield in both batches were very similar. Probably the agitation of the system facilitates the mass transfer in the bioreactors and favors the biogas production.

Table 2: Biomass characterization after digestion and estimation of the final organic matter destruction.

Agitated bioreactors					
	pH	**Volatile Matter (%)**	**Ashes (%)***	**Chromium (%)***	**Organic Matter Destruction (%)**
Blank	8.07	97.9 ± 0.5	61.2 ± 0.2	0.9 ± 0.0	-
CTLW	8.50	94.7 ± 0.2	36.0 ± 0.1	2.2 ± 0.0	27.0 ± 0.4
E170W	8.56	96.2 ± 0.0	53.7 ± 0.1	3.9 ± 0.5	76.7 ± 1.4
E100D	8.57	95.7 ± 0.7	54.9 ± 0.6	2.2 ± 0.1	71.8 ± 0.4
Non-agitated bioreactors					
	pH	**Volatile Matter (%)**	**Ashes (%)***	**Chromium (%)***	**Organic Matter Destruction (%)**
Blank	8.05	97.8 ± 0.0	59.4 ± 0.6	0.6 ± 0.1	-
CTLW	8.58	95.1 ± 0.0	38.3 ± 0.2	2.1 ± 0.1	37.6 ± 2.4
E170W	8.65	96.4 ± 0.0	53.6 ± 0.1	3.1 ± 0.3	81.4 ± 0.5
E100D	8.66	96.5 ± 0.1	54.3 ± 0.1	2.1 ± 0.0	81.2 ± 0.1

*Dry basis; mean ± standard deviation, n = 3

The characterization of the final sludge enabled the estimation of the final organic matter destruction (Table 2). The extruded samples presented organic matter destruction between 70% and 82%, a very high destruction of the original substrate, while the untreated sample could only reach 27% to 38%. This indicates that the CTLW is a complex substrate and the pre-treatments are very important to assure the reduction of the final wastes.

4. CONCLUSION

Three different pre-treatments were carried out to ease the anaerobic digestion of chromium tanned leather shavings. The evaluation of the pre-treated samples showed that it is possible to increase the degradability of the wates, reaching more than 90% of degradation by trypsin in the cases of the autoclaved and hydrothermally treated samples, and 35% for the extruded samples.

In the biogas production trials with extruded samples the pre-treatment decreased the onset time of biogas production of the leather shavings by 5 days. The extruded samples also presented higher biogas yields when compared to the untreated sample, reaching up to 370 l_N.kgo_D while the latter could only reach 233 l_N.kgo_D. The agitated trials were proven to have a better performance for the tested pre-treated samples, facilitating the mass transfer inside the reactors. The extrusion pre-treatment also increased the leather destruction while producing biogas. It was possible to destruct approximately 80% of the pre-treated samples.

Results up to now show that the pre-treatments can increase the efficiency of the biogas production out of chromium tanned leather shavings. The pre-treatments accelerate the process and improve the final yield apart from enhance the wastes destruction. All these improvements increase the suitability of this method for the industry.

5. ACKNOWLEDGEMENTS

The authors would like to thank DAAD (German Academic Exchange Service) for the financial support of this work.

6. REFERENCES

Agrawal A, Kumar V, Pandey B D, Remediation options for the treatment of electroplating and leather tanning effluent containing chromium – A review, Mineral Processing and Extractive Metallurgy Review, 2006, **27**, 99–130.

Agustini C, Neto W, Costa M, Gutterres M, Biodegradation and biogas production from solid waste of tanneries, XXXIII IULTCS Congress, Novo Hamburgo, Brazil, 2015.

Avery N C, Bailey A J, Restraining cross-links responsible for the mechanical properties of collagen fibers: natural and artificial; In: Fratzl P. (Ed.). Collagen: structure and mechanics, Springer, New York, 2008.

Banu J R, Kaliappan S, Treatment of tannery wastewater using hybrid upflow anaerobic sludge blanket reactor, Journal of Environmental Engineering and Science, 2007, **6**, 415-421.

Covington A D, Tanning Chemistry: The Science of Leather, The Royal Society of Chemistry, Cambridge, 2009.

Deublein D and Steinhauser A, Biogas from Waste and renewable Resources; An Introduction, Wiley-VCH, Weinheim, 2008.

Dhayalan K, Fathima N N, Gnanamani A, Rao J R, Nair B U, Ramasami T, 2007. Biodegradability of leathers through anaerobic pathway. Waste Management, 2007, **27**, 760–767.

Ferreira M J, Almeida M F, Pinho S C, Santos I C, Finished leather waste chromium acid extraction and anaerobic biodegradation of the products, Waste Management, 2010, **30**, 1091–1100.

Fratzl P, Collagen: structure and mechanics; an introduction, chapter 1; In: Fratzl P. (Ed.). Collagen: structure and mechanics, Springer, New York, 2008.

GROW - Informatics unit - EDW team, Estimations of structural data – Leather, 2016.

Hulmes D J S, Collagen diversity, synthesis and assembly, chapter 2; In: Fratzl P. (Ed.). Collagen: structure and mechanics, Springer, New York, 2008.

IULTCS, IUE4: Assessment for chromium containing waste from leather industry, 2008.

Kameswari K S B, Kalyanaraman C, Porselvam S, Thanasekaran K, Optimization of inoculum to substrate ratio for bio-energy generation in co-digestion of tannery solid wastes, Clean Technologies and Environmental Policy, 2012, **14**, 241–250.

Kameswari K S B, Kalyanaraman C, Thanasekaran K, Effect of ozonation and ultrasonication pretreatment processes on co-digestion of tannery solid wastes, Clean Technologies and Environmental Policy, 2011, **13**, 517–525.

Kameswari K S B, Kalyanaraman C, Thanasekaran K, Evaluation of various pre-treatment processes on tannery sludge for enhancement of soluble chemical oxygen demand, Clean Technologies and Environmental Policy, 2014, **16**, 369–376. (a)

Kameswari K S B, Kalyanaraman C, Thanasekaran K, Optimization of organic load for co-digestion of tannery solid waste in semi-continuous mode of operation, Clean Technologies and Environmental Policy, 2015, **17**, 693–706.

Kameswari K S B, Kalyanaraman C, Umamaheswari B, Thanasekaran K, Enhancement of biogas generation during co-digestion of tannery solid wastes through optimization of mix proportions of substrates, Clean Technologies and Environmental Policy, 2014, **16**, 1067–1080. (b)

Kolomaznik K, Adamek M, Andel I, Uhlirova M, Leather waste - Potential threat to human health, and a new technology of its treatment, Journal of Hazardous Materials, 2008, **160**, 514–520.

Marin J, Kennedy K J, Eskicioglu C, Effect of microwave irradiation on anaerobic degradability of model kitchen waste, Waste Management, 2010, **30**, 1772–1779.

Mata-Alvarez J, Dosta J, Romero-Güiza M S, Fonoll X, Peces M, Astals S, A critical review on an aerobic co-digestion achievements between 2010 and 2013, Renewable and Sustainable Energy Reviews, 2014, **36**, 412–427.

Mu C, Lin W, Zhang M, Zhu Q, Towards zero discharge of chromium-containing leather waste through improved alkali hydrolysis, Waste Management, 2003, **23**, 835–843.

Murphy J and Thamsiriroj T, Fundamental science and engineering of the naerobic digestion process for biogas production, chapter 5. In: Wellinger A., Murphy J. and Baxter D. (Ed.), The biogas handbook, Woodhead Publishing Limited, Cambridge, 2013.

Pati A, Chaudhary R, Subramani S, A review on management of chrome-tanned leather shavings: a holistic paradigm to combat the environmental issues, Environmental Science and Pollution Research, 2014, **21**, 11266–11282.

Ravindranath E, Chitra K, Porselvam S, Srinivasan S V, Suthanthararajan R, Green energy from the combined treatment of liquid and solid waste from the tanning industry using an upflow anaerobic sludge blanket reactor, Energy Fuels, 2015, **29**, 1892−1898.

Schuberth-Roth V T, Erster Schritt in neue Energie-Ära, Frankenpost, Rehauer Tagblatt, 2013.

Shanmugam P, Horan N J, Optimising the biogas production from leather fleshing waste by co-digestion with MSW, Bioresource Technology, 2009, **100**, 4117–4120.

Thangamani A, Parthiban L, Rangasamy P, Two-phase anaerobic digestion model of a tannery solid waste: experimental investigation and modeling with ANFIS, Arabian Journal for Science and Engineering, 2015, **40**, 279–288.

Thangamani A, Rajakumar S, Ramanujam R A, Anaerobic co-digestion of hazardous tannery solid waste and primary sludge: biodegradation kinetics and metabolite analysis, Clean Technologies and Environmental Policy, 2010, **12**, 517–524.

VDI 4630, Fermentation of organic materials, Characterization of the substrate, sampling, collection of material data, fermentation tests, The Association of German Engineers, Düsseldorf, Germany, 2006.

Wess T J, Collagen fibrillar structure and hierarchies, chapter 3; In: Fratzl P (Ed.). Collagen: structure and mechanics. Springer, New York, 2008.

Zupancic G D, Jemec A, Anaerobic digestion of tannery waste: Semi-continuous and anaerobic sequencing batch reactor processes, Bioresource Technology, 2010, 101, 26–33.

SFS O-22

SUSTAINABLE LEATHER MANAGEMENT: A MASS BALANCE BENCHMARK OF DIFFERENT CHROMIUM TANNING TECHNOLOGIES

Dietrich Tegtmeyer*, Volker Rabe, Martin Kleban, Christopher Tysoe

LANXESS Deutschland GmbH, 51369 Leverkusen, Germany, dietrich.tegtmeyer@lanxess.com
LANXESS Deutschland GmbH, 51369 Leverkusen, Germany, volker.rabe@lanxess.com
LANXESS Deutschland GmbH, 51369 Leverkusen, Germany, martin.kleban@lanxess.com
LANXESS Deutschland GmbH, 51369 Leverkusen, Germany, christopher.tysoe@lanxess.com

Chrome tanning remains the best known available technology to thermally stabilize collagen, the main structural protein of any hide or skin. Multiple research studies of all mineral tanning processes over several years have shown that Cr III sulfate performs best due to two key reasons: 1. The Cr III ion forms an extremely stable complex with the inner structure of the protein triple helix, and 2. The tanning production process of penetration and fixation is easily controlled.

Tanners have traditionally focused, arguably quite logically, in the first instance on the quality of the resulting wet blue and crust leather and thus designed the process accordingly. This unfortunately has resulted in tanning processes commonly not being optimized in terms of efficiency and sustainability. Approximately only 40% of the initially offered amount of chrome tanning material (CTM) ends up in the final leather. The remainder (i.e. up to 60%) of the CTM is either washed during processing, or is in the solid waste, mainly shavings. Recycling is possible for most of this "waste." Chrome containing sludge can be safely, legally and usually economically disposed of, so it is acceptable from an environmental perspective. However, from a sustainability point of view (and most probably also from a longer-term economic view), this endless "dumping" of finite resources needs to be questioned, and the sooner the better.

In the following article, two alternatives to the "standard" chrome tanning process are discussed. High-exhaustion technology and/or hybrid tanning technology would lead not only to a major improvement in the mass balance for chrome tanning material, it would also in turn be of immediate benefit in terms of the public perception of the leather sector and most probably also critical for the long-term future of the entire tanning industry.

Keywords: chromium, tanning, mass balance, effluent, waste, exhaustion

1. INTRODUCTION

The main "operating" step in leather manufacturing is the tannage, which stabilizes the collagen and chemically converts this protein into leather. Due to the ideal chemical characteristics of chromium in the valence state III, this element can enter inside the triple helical structure of collagen where it uses its special complexing and cross-linking behavior to stabilize the protein matrix. The geometric dimensions of the resulting Cr(III) complex fits in perfectly with the surrounding 3-D protein structure of the collagen. The macroscopic result is a significant increase of the denaturation point (= shrinking temperature) of the leather above 100 °C that can only be achieved with a chrome tanning material (CTM) and not with any other metal tanning agent on its own. Decades of research were necessary to understand the ideal, complex chemistry of chrome tanning scientifically and several theories have been developed which explain the different phenomena of this process step. One famous theory is the principle of covalent tanning with chrome tanning materials (CTM) within the link-lock mechanism (1). Another important and fundamental finding is the principle of olation/oxolation of metal ions (2).

1.1. The principle of olation

Reference is often made to the cross-linking of CTM, and rather less frequently to olation, a type of “in-situ” inorganic polymerization (3), but this is still fundamental and critical for understanding the tanning process. At a low pH (i.e. “pickle”) many metal ions exist in solution as complexes with a low molecular weight that are unreactive or rather less reactive to collagen. As the pH increases (i.e. “basification”), these complexes start to react with each other to form larger molecules (metal ion oligomers) with higher reactivity towards the collagen subunits, up to a level where they become insoluble. The tendency is to form bigger molecules rather than cross-linking collagen, up to a level where no reaction with the protein takes place anymore, and the ability to steer this with suitable ligands depends on the nature of the metal. Here, only chrome(III) has the right pH-dependent balance between increasing both molecular weight to the right size and reactivity toward collagen, also steering this easily with suitable ligands like sulfate or acetate.

1.2. Other mineral tanning technologies

It is known that other metals can provide a stabilization effect such as aluminum, zirconium or iron, to name the most important ones in order of tanning power. The stabilization effects follow a different mechanism as described in (1) and even the pH-dependent olation/oxolation phenomenon (3) has different (for leather tanning unfavorable) characteristics. Subsequently, all these alternative metal tanning systems result also in a lower denaturation point of the resulting substrate. So far, no alternative tanning agent for leather exists that fulfills the unique property profile of CTM. Therefore, non-chrome systems usually require some degree of “compensation” especially in the retanning step. This results in additional amounts of conventional retanning chemicals being required, thus changing sustainability profile and haptic and technical performance, although application-wise a chrome-like character is possible.

1.3. Advantages and challenges of the chrome tanning process

The chrome tanning process is the dominant tanning system also because it is a relatively easy, stable and robust process. It results reliably in a safe, high-performance technical substrate. The speed of penetration of CTM can be easily steered via simple measures and controlled even visibly. The following process step involving the cross-linking reaction of the chromium in the leather can again mainly be managed by pH adjustment with harmless basification agents. Thus about 85% of the world’s leather production is still based on chrome-tanned leather, and this has been the case for more than 100 years and is expected to continue in the foreseeable future.

To continue the future-proof development of chrome tanning both in general and especially from a sustainability point of view, a closer look at two important aspects is required. First: process rules to avoid the formation of Cr VI in leather. Second: process concepts to increase the utilization of CTS further in order to keep the release of chromium into the effluent to an absolute minimum.

For the first topic, clear process rules to be followed have already been established and are well known as a best available technology (3). In order to have a closer look at the second topic, a simple mass balance needs to be performed to compare different chrome tanning process alternatives.

2. MASS BALANCE OF DIFFERENT CHROME TANNING PROCESSES

Here, the mass balance of three different process alternatives is compared and all should result, with relatively minor adjustments of the retanning recipe, in similar crust articles:

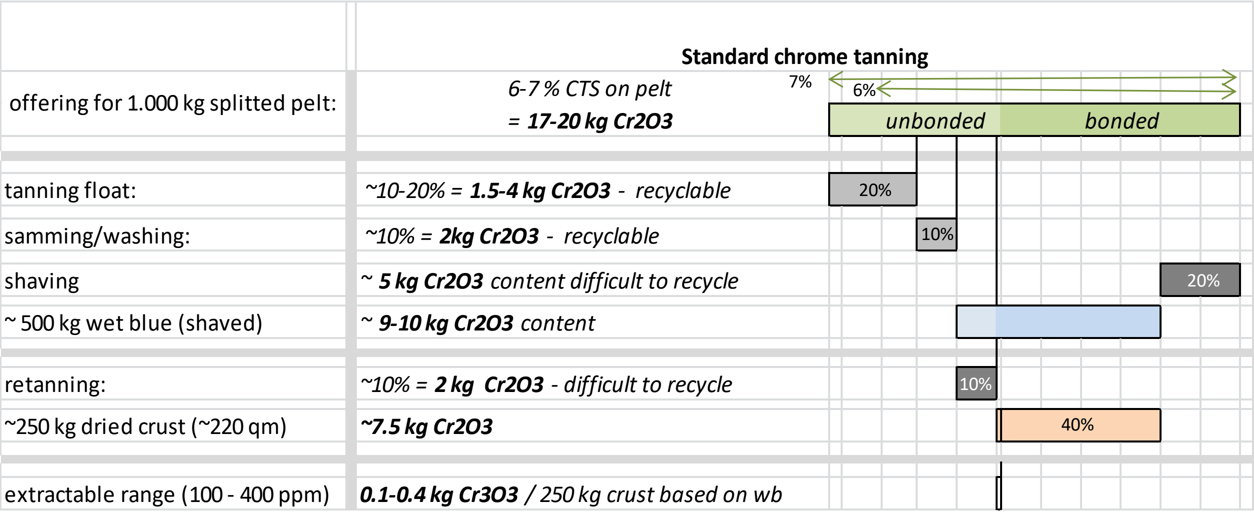
1. Standard chrome tanning
2. High-exhaustion chrome tanning
3. Hybrid tanning – wet white pre-tanning with high-exhaustion re-chroming

2.1. Standard chrome tanning process

In a standard chrome tanning operation, initially up to 8% of CTM is offered (in relation to pelt weight – Table 1), corresponding to an absolute amount of 17-20 kg Cr2O3 based on 1,000 kg pelt. About 60% of this chromium will be chemically fixed (via covalent bonding) to the protein while approx. 40% remains still unfixed (either in the float or in the liquid within the leather matrix after the tanning operation). During the subsequent washing and processing steps (samming, retanning), about 40% of the initially offered CTM will be washed out in the effluent and should be separated by further treatment. In a modern tannery operation, the majority of this discharge could be separated and recycled. However, good equipment and especially proper and intensive quality controls of the recycled chrome material are necessary to ensure that the quality of the wet blue is comparable to the usage of only CTM from a reliable supplier. If the chrome is not recycled it must be safely and legally deposited at appropriate, usually municipal, approved facilities.

Furthermore, up to approx. 20% of the initially offered CTM will end up in the solid waste as shavings. The majority of the chrome in the shavings will either end without a specific functional requirement in an upstream basic raw material (e.g. for construction or energy generation) or again end up on as waste in a landfill.

Considering these two “losses” in a normal retanning process, without additional re-chroming only around 40% of the initially offered amount of CTM ultimately ends up in the final leather. From this remaining chromium in the final leather matrix only a very small part (some ppm) is not strongly bonded and can be extracted with artificial sweat from the dried crust leather. This is what is usually referred to as the “leachable” chrome part.



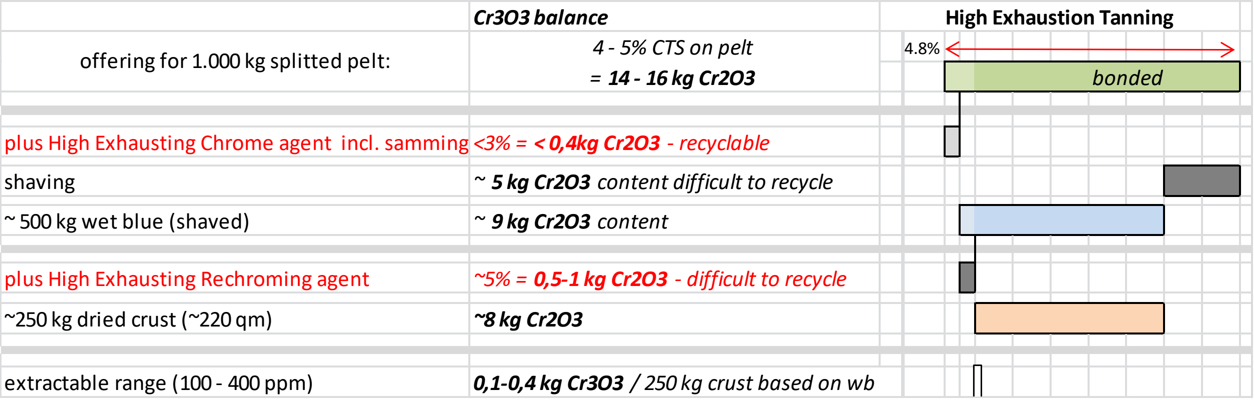
	Standard chrome tanning
offering for 1.000 kg splitted pelt:	*6-7 % CTS on pelt* *= **17-20 kg Cr_2O_3***
tanning float:	*~10-20% = **1.5-4 kg Cr_2O_3** - recyclable*
samming/washing:	*~10% = **2kg Cr_2O_3** - recyclable*
shaving	*~ **5 kg Cr_2O_3** content difficult to recycle*
~ 500 kg wet blue (shaved)	*~ **9-10 kg Cr_2O_3** content*
retanning:	*~10% = **2 kg Cr_2O_3** - difficult to recycle*
~250 kg dried crust (~220 qm)	***~7.5 kg Cr_2O_3***
extractable range (100 - 400 ppm)	***0.1-0.4 kg Cr_3O_3** / 250 kg crust based on wb*

Table 1: Mass balance of a standard chrome tanning process

2.2 High-exhaustion chrome tanning process

As an alternative to standard chrome tanning processes, in Table 2 the mass balance of a typical high-exhaustion chrome tannage is illustrated. The sustainability is considerably improved, because the majority of chrome originally offered ends up in the leather. Furthermore, this process can be run with the same equipment as the standard chrome tanning process; no special investment needs to be made and in principle every tannery worldwide should be able to switch to a high-exhaustion process.

As less chromium will be washed out into the effluent with this high-exhaustion process, the initial offer can be reduced down to 4.5 - 5% (based on pelt weight). This alone represents an almost quarter reduction in CTM use compared to the standard process. Through the addition of special fixing agents – high-exhausting chrome tanning agents – the exhaustion can be improved significantly, not only in the tanning, but also in the retanning process step. Subsequently, the resulting amount of chrome in the raw effluent is so low that most legal requirements for the chromium content of the discharge can be met without any problem. This process also results in a high score in the Leather Working Group (LWG) audit, which requires an uptake of at least 97%. The total amount of chromium in the final leather is comparable to the standard chrome tanning process. The key difference is that the unfixed proportion, which normally gets washed out during processing and ends up in the effluent in the standard process, is effectively eliminated.



	Cr_3O_3 balance	**High Exhaustion Tanning**
offering for 1.000 kg splitted pelt:	*4 - 5% CTS on pelt* *= **14 - 16 kg Cr_2O_3***	
plus High Exhausting Chrome agent incl. samming	*<3% = **< 0,4kg Cr_2O_3** - recyclable*	
shaving	*~ **5 kg Cr_2O_3** content difficult to recycle*	
~ 500 kg wet blue (shaved)	*~ **9 kg Cr_2O_3** content*	
plus High Exhausting Rechroming agent	*~5% = **0,5-1 kg Cr_2O_3** - difficult to recycle*	
~250 kg dried crust (~220 qm)	***~8 kg Cr_2O_3***	
extractable range (100 - 400 ppm)	***0,1-0,4 kg Cr_3O_3** / 250 kg crust based on wb*	

Table 2: Mass balance of a high-exhaustion chrome tanning process

2.3 Hybrid tanning technology – wet white pre-tanning followed by high-exhaustion re-chroming

With the term “hybrid tanning technology” we refer to the combination of wet white pretanning with a synthetic tanning agent. For the most sustainable wet white technologies (e.g. ref. 3) there is even no need to pickle. Obviously, no chromium can end up in the effluent, or any by-products such as shavings; the process up to the wet white intermediate stage is completely free of chrome.

In order to get a similar intermediate like a wet blue, the retanning process then has to start with a re-chroming step. A high-exhausting re-chroming agent is added, approx. 5-7% based on shaved wet white weight, which correlates to only around 2-2.5 kg absolute Cr2O3 based on 1,000 kg split pelt. (Shaved wet weight has about 30-50% of the weight of a pelt, depending on water content and shaved thickness.)

With a special fixing re-chroming agent the exhaustion in this process step is extremely high. Close to 100% of the initially offered Cr2O3 ends up in the crust leather, with only a tiny amount of Cr2O3 washed out in the retanning floats. Visible for all by their lack of color, these floats are correspondingly virtually colorless and transparent. After re-chroming, the typical organic retanning process completes the process, usually with only slight adjustments in the recipe being necessary in order to reach a similar crust to that achieved with a traditional wet blue intermediate.

	High-exhaustion rechroming	
offering for 1.000 kg splitted pelt:	*5-7% RC on* ***ca. 2-2,5 kg Cr2O3***	🟩
tanning float:		
samming/washing:		
shaving		
~ 500 kg wet blue (shaved)		
retanning:	***< 0.5 kg Cr2O3***	▮
~250 kg dried crust (~220 qm)	***ca. 2 kg Cr2O3***	🟧

Table 3: Mass balance of a hybrid tanning process – wet white pre-tanning followed by a high-exhaustion re-chroming process

2.4 Discussion of the three chrome tanning processes

The comparison of the mass balances of the three tanning processes show that, from a sustainability point of view, the two suggested alternative processes are more favorable compared to the standard chrome tanning process. Since there are so many parameters that can influence the outcomes, such as local conditions, recipes, raw material quality, beamhouse preparations, etc. we have purposely entered only rough numbers for chromium content in the effluent. However, many production-scale examples have shown that running a high-exhaustion process already reduces the chromium content of the effluent to such an extent that in most cases the effluent can be discharged directly to a wastewater treatment plant without any pre-treatment or chrome separation required. Also in the case of sludge, it has such a low chromium content that it is not considered to be a hazardous chemical (according to most of the legal requirements). This already is a considerable process achievement.

In our industry today there still remains the issue of Cr-containing shavings, which concerns massive volumes. The ultimate sustainable process and best available compromise where you still have all the advantages of a chrome-tanned article without this issue is considered to be the “hybrid tanning process.” Zero chrome in the effluent and the shaving byproduct is obviously guaranteed during a wet white pre-tanning step. With the use of a special high-exhausting re-chroming agent, the leather will virtually fix all offered active chromium ions afterwards; therefore nearly all offered amounts of chromium will end up in the final leather sold, and not in any waste.

3. CONCLUSION

Stainless steel can be produced only with chromium, i.e. there is no other element in the periodic system which gives a similar stabilization of the iron. Similarly in leather making there is no other known technical possibility of stabilizing the protein than in a chrome-tanned leather. There are different ways to chrome tan a leather. In order to strive for the best available sustainability performance it has been shown that the two proposed alternatives to standard chrome tanning would provide an interesting sustainable opportunity: either a high-exhaustion chrome tanning process including a downstream use for the wet blue shavings, or – even better – a wet white retanning process followed by a shaving and a re-chroming step of the shaved material. In both cases the overall material mass balance would be improved. Depending on adjustments in the retanning process. even the resulting final crust in all three articles would be comparable.

References:

1. A.D. Covington et al., World Leather, October/November 2010.
2. Helm, L. and Merbach, A. E., "Inorganic and Bioinorganic Solvent Exchange Mechanisms", Chem. Rev., 2005, 105, 1923-1959.doi:10.1021/cr030726o.
3. Holleman, A. F.; Wiberg, E. "Inorganic Chemistry" Academic Press: San Diego, 2001. ISBN 0-12-352651-5.
4. CADS – Der Leitfaden für Lederhersteller / Guiding principles for leather manufacturer; www.cads-shoe.com
5. N. Brinkmann, J. Reiners, D. Tegtmeyer, C. Tysoe,, IULTCS Congress 2011, Istanbul

SFS O-23

FORMALDEHYDE AND ACETALDEHYDE ON LEATHER: SIMILARITIES AND DISCREPANCIES

Jochen Ammenn*, Brigitte Wegner, Bernd Dannheim

BASF SE, Ludwigshafen, Germany

*Email: jochen.ammenn@basf.com

Formaldehyde and leather have a relation of over one hundred years, since formaldehyde is a very common building block for the synthesis of syntans and resins and has even been used for tanning as such. While there is a lot of literature and best practice around how to minimize formaldehyde in leathers on the basis of extraction methods, acetaldehyde is not used as a building block and rarely appears in extraction assays. However, it contributes to significant problems in emission test for automotive leathers, especially to meet the standards in the Chinese market. This article will reveal new emission data assembled by new measurements. A new, facile method will be introduced and exemplified with data across the process of leather making, from tanning to finished leather and across various chemistries applied.

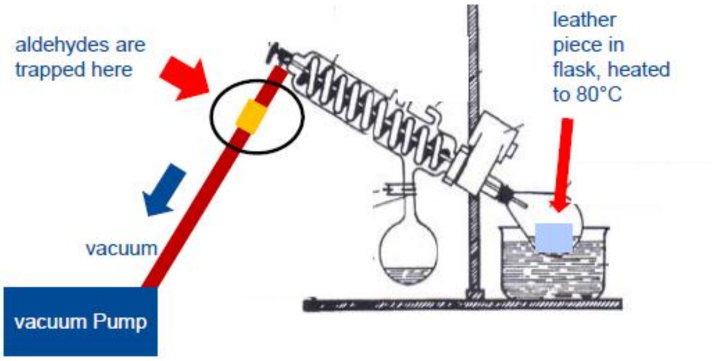
Keywords: Formaldehyde, acetaldehyde, emission, scavenging.

1. Introduction

While formaldehyde is a widely used building block for the synthesis of syntans and resins in leather (1), acetaldehyde is a natural product, not used in the process of leather making. While acetaldehyde has not created problems after extraction measurements of leather according to ISO 17226, it does appear in emission tests and the results created concerns (2), especially in automotive leather for the Chinese market, due to Chinese legislation: GB/T 27630-2012. So far, there are several emission chamber tests on the market, but the results are difficult to compare and only few data points about acetaldehyde emission can be created since the measurement takes several hours. We established a method for acetaldehyde emission suitable for screening to gain insights not only on finished leather, but also within the process of leather making and in order to compare the contribution of products.

2. Material and Methods

In VDA 275 aldehyde emission can be detected from water, stored on the bottom of a bottle with a piece of leather above the water. In these tests only a few ppm acetaldehyde are detected. In case of chamber emission measurements, the leather is conditioned in a closed chamber and the air is removed and analyzed for aldehydes. In these measurements significant values of acetaldehyde are detected. Automotive companies use these chambers to analyze volatile organic compounds either with raw material for the interior of cars, such as finished leather, textiles, or plastic, or with already assembled parts for the interior of cars. We developed a chamber on the basis of a rotation evaporator in which pieces of leather can be analyzed. The leather remains in the closed apparatus at 80°C water bath temperature and remains there for thirty minutes. Finally, the air is removed from the chamber via evaporation pump and aldehydes are derivatized to their dinitrophenyl hydrazones in a cartridge (3) positioned between the rotation evaporator and the pump, as shown in scheme 1. The hydrazone is washed off the cartridge and quantified via calibration curve on a HPLC.



Scheme 1. Acetaldehyde determination in a rotation evaporator

3. Results and Discussion

Initial measurements revealed that the acetaldehyde emissions are highest in the early stages of leather making like wet blue and are minimized on crust basis. It should be taken into account that the water content in wet blue is significantly higher than in crust. After finishing acetaldehyde emissions rise marginally, as can be seen in figure 1.

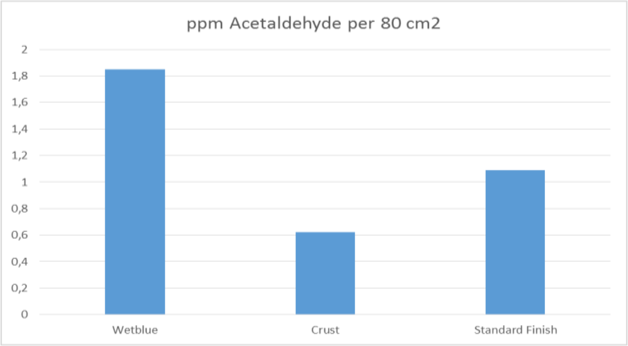


Figure 1. Acetaldehyde emission in three stages of the leather making process

These findings are similar within the wet white process. Although the boiling point of acetaldehyde is only twenty one degree Celsius the emissions from the leather do not minimize over time. In a long term study with finished leather the values of acetaldehyde emissions stayed the same in a period of ten month, as depicted in figure 2.

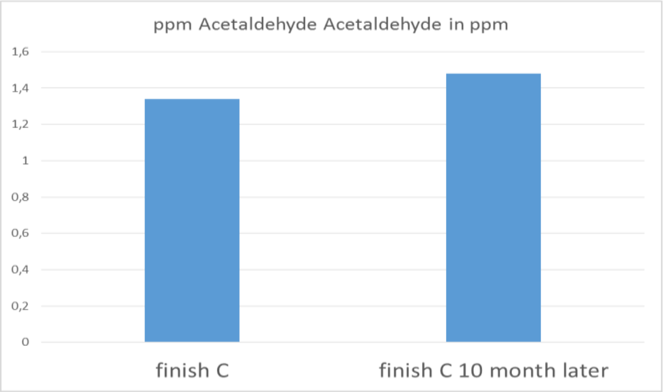


Figure 2. Acetaldehyde emission over time

Comparison of various wet end products like syntans, polymers, resins, or vegetable tannins did not reveal significant differences. This is why we focused on process modifications. In a study with three vacuum evaporations within the leather making process until crusting, about a 30% reduction of acetaldehyde emissions was achieved, compared to a leather made with only one evaporation after crusting. In this modified process, vacuum was applied once on wet blue, a second time in the middle of the wet end process between re-tanning and fat-liquoring and a third time after crusting. Results are shown in figure 3.

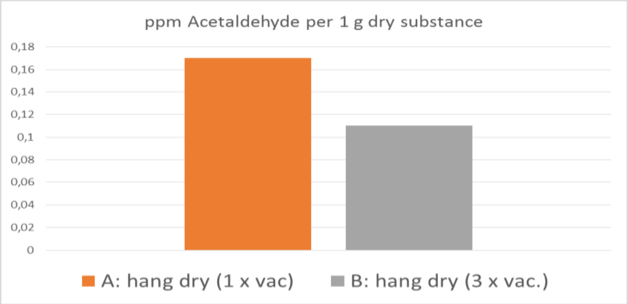


Figure 3. Reduced acetaldehyde emission after three evaporation, compared to one evaporation after crusting

The acetaldehyde emission were undertaken not directly after the vacuum on crust basis, but after a subsequent twelve hours hang drying in order to re-establish a comparable dry content. The dry content has a significant impact on acetaldehyde emission.

Scavenging substances for acetaldehyde were screened for emission reduction, but only few showed significant and reproducible results. As depicted in figure 4, a scavenger that was applied in a flesh side treatment via spraying on finished leather lead to a 30 % reduction of emissions.

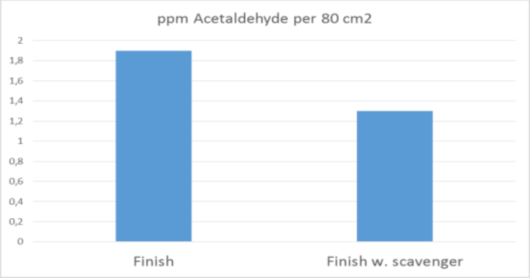


Figure 4. Reduced acetaldehyde emission after flesh side application of a scavenger via spraying compared to the untreated finished leather.

The same amount of scavenger applied in wet end did not lead to the same results, as achieved with flesh side application on finished leather.

Interestingly, acetaldehyde occurs in nature in the degradation of glucose and of threonine by microorganisms. However, while it is well possible that these microorganisms exist in the raw hide and produce acetaldehyde there, the possibility that these microorganisms survive the beam house and continue to function later stage in leather, is difficult to imagine.

4. Conclusion

We established a method to monitor the acetaldehyde emission within the process of leather making and on product basis by comparing different products on a one to one basis. While emissions are high in early stages, like wet blue, they are minimized on crust basis. After finishing acetaldehyde emissions rise marginally. Comparison of wet end products did not lead to significant reduction of emission. This is why we focused on process modifications. Applying vacuum three times in crusting compared to one time, lowered the emissions. However, this process modification adds complexity to the leather production process. Through application of a scavenger on the flesh side of finished leather, promising results were achieved.

While formaldehyde occurs in extraction analysis, if products with high formaldehyde content are used within the leather making process, acetaldehyde is not used as a building block, but appears in emission test. We managed to reduce acetaldehyde emissions via process modification and scavenging but the chemical / bio-chemical source of acetaldehyde remains to be discovered.

5. Acknowledgements

This work was initially a joined effort between BASF and the FILK research Institute in Freiberg, Germany. We wish to thank Bernd Matthes and Haiko Schulz for their collaboration.

6. References

1. Ammenn, J.; Huebsch, C.; Schilling E., Dannheim, B.; Chemistry of Syntans and their Influence on Leather Quality, *JALCA,* 2015, Vol. 110, p. 349 – 354.2
2. Spengler, John D.; McCarthy, John F.; Samet, Jonathan M.; 2000. *Indoor Air Quality Handbook*. New York, NY, USA: McGraw-Hill Professional Publishing. ISBN 0074455494. p 761.
3. Herrington J.S.; Fan Z., Lioy P.J.; Zhang J.J.; Environmental Science & Technology, 2007, 41, 580-585.

SFS O-24

REDEFINING CHROME TANNING: A WATERLESS APPROACH

P. Thanikaivelan*, R. Aravindhan, B. Madhan, GC. Jayakumar, P. Saravanan & J. Raghava Rao

CSIR-Central Leather Research Institute, Adyar, Chennai 600020
Email: jrrao_clri@yahoo.co.in

Leather is one of the most important commodities used globally for various applications with an annual trade of 120 billion USD. However, leather-processing industries are recognized as one of the major polluting sector. Conventional way of leather making is water intensive, in which 25-50 liters of water is employed for processing 1 kg of hides/skins. Although several technological options are available to reduce the water consumption, the volume of water used for leather manufacturing is still in higher order. It is projected that about 1.8 billion people will live in countries or regions with absolute water scarcity by 2025 AD. As water scarcity is emerging as a major threat for future generation, minimization of usage gains highest importance. Therefore, water usage and wastewater generation in industrial processes would be a sensitive issue in future and it is imperative to develop 'zero water use technologies'. Use of no water for chrome tanning does not only facilitate minimization of water but also provide a viable solution to the problem of chromium pollution. However, 'waterless chrome tanning' is highly challenging, as water is the best solvent for the transportation of chromium into hide network. The strategies adopted for waterless tanning include exploiting the matrix water for achieving the penetration of chromium into hide network. The developed technology has already been validated and commercialized and translated to many tanneries. The benefits are many folds, which include cost reduction, pollution reduction, avoidance of pickling and basification and finally improved quality of leather. In addition to the above benefits, the developed approach would provide a new paradigm in 'leather science', in particular, to the century old 'chrome tanning'.

INTRODUCTION

Generation of huge quantities of wastewater is a major concern for leather manufactures around the world.[1] Chrome tanning leads to as high as 1500-4000 ppm of trivalent chromium containing wastewater along with about 15000-50000 ppm chlorides.[1, 2] Use of common salt during pickling process leads to high total dissolved solids (TDS) and chlorides generation.[3] Environment regulating agencies are very stringent on the discharge of chromium and TDS and they stipulated norm of 2 and 2100 ppm, respectively for the release of tannery effluent to inland water bodies.[4] Several chrome management systems such as high exhaust chrome tanning,[2] pickle-basification free chrome tanning,[3, 5-7] direct chrome liquor recycling,[8] chrome recovery and reuse[9] systems were developed. The use of chrome exhaust aids,[10] less chrome,[11] chrome-free[12, 13] and alternative medium[11, 14] based technologies have also been developed to meet the regulatory norms.

Research Initiatives for Waterless Tanning (RIWT) is one of the projects of XII Five Year Plan Period of CSIR-CLRI. The core objective of the project is to study, understand and explore the possibility of a) use of alternative eco-friendly medium for leather manufacturing process and b) use of medium. Water is required for the hydrolysis of chromium(III) species in order to initiate strong binding with the carboxyl functional groups in collagen and hence it is a challenging task to perform chrome tanning without water. Studies to understand the possibility of using green solvents, ionic liquids and supercritical carbon dioxide in place of water have been conducted. The role played by water as a medium in the transportation of chemicals into the hide network has also been understood. This scientific epiphany incited to experiment the tanning process sans water or any other medium. It became conspicuous that by fulfilling certain process requirements, it was possible not to use water for chrome tanning. The designed process also brought about the benefit of doing away with the unit process of pickling. And therefore, there is a matching benefit of reduction of salinity and total dissolved solids (TDS). The process accordingly designed had been experimented and perfected initially at laboratory scale and then at pilot scale. Taking into considerations, the requirements of shop floor, the process was fine-tuned and standardized at commercial scale. The influence of the process on the properties of the immediate product that is wetblue and the final process that is finished leather has also been studied.

PILOT SCALE STUDIES TO FIND THE ROLE OF PROCESS WATER IN CHROME TANNING

This study is an attempt to revolutionalise the currently employed chrome tanning methods to completely eliminate chromium effluent by enhancing water economy during chrome tanning process. Notionally, no effluent is let out after chrome tanning. The conventionally delimed cow pelts were pre-treated suitably to make the matrix weakly anionic or non-ionic state.[15] Then the pelts were treated using Basic Chromium Sulfate (BCS) of 33% basicity. No water was administered during the tanning process. Because of the non-availability of water, much of the BCS is in anionic state. The chromium is transported into the hide network due to the concentration gradient created. Additional chemical auxiliaries were added to facilitate the penetration. Once the chromium is penetrated, it undergoes hydrolysis very slowly and binds with skin/hide matrix. For the chromium to get fixed, the matrix water was found to be sufficient. And therefore, chemicals such as sodium bicarbonate are not needed for fixing the chromium with the pelt. In the initial trials, process water was varied as 0, 25, 50, 75 and 100% and chrome tanning was carried out using 7% BCS.

Experimental leathers were characterized for chrome content, hydrothermal stability and strength properties. Shrinkage temperature of experimental leathers were in the range of 108-111°C, as seen in Table 1, which was similar to conventional chrome tanned leathers. The exhaustion of chromium is near 100% at 0% float. Organoleptic properties ascertain that there were no patches and leathers appeared like conventional tanned wet blue with smooth grain even at zero float (Figure 1). It is seen that the chromium is distributed uniformly in all the layers and the amount of chromium is higher when the float is very low or zero (Figure 2). Physical strength characteristics meet UNIDO norms, which assure the required characteristics for end applications (data not shown). The study reveals that the chrome tanning can be carried out without any float. Therefore, this methodology provides zero discharge of chrome tanning effluent, as there is no process water employed for chrome tanning, thereby providing an ecofriendly tanning system.

Table:1 Percentage exhaustion and shrinkage temperature

Float (%)	Exhaustion (%)	Shrinkage Temperature (Ts °C)
0	**98**	**108**
25	95	109
50	90	111
75	89	108
100	87	109

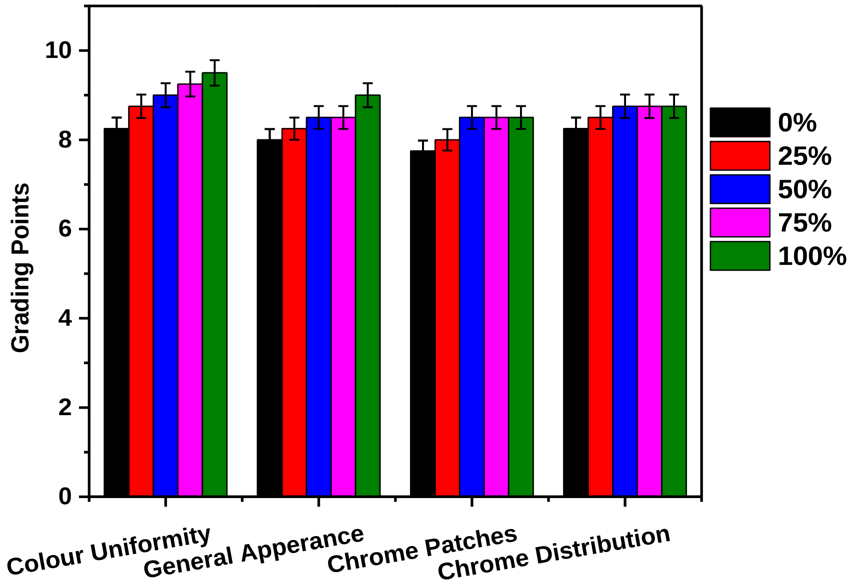


Figure 1. Characteristics of wet blue leathers

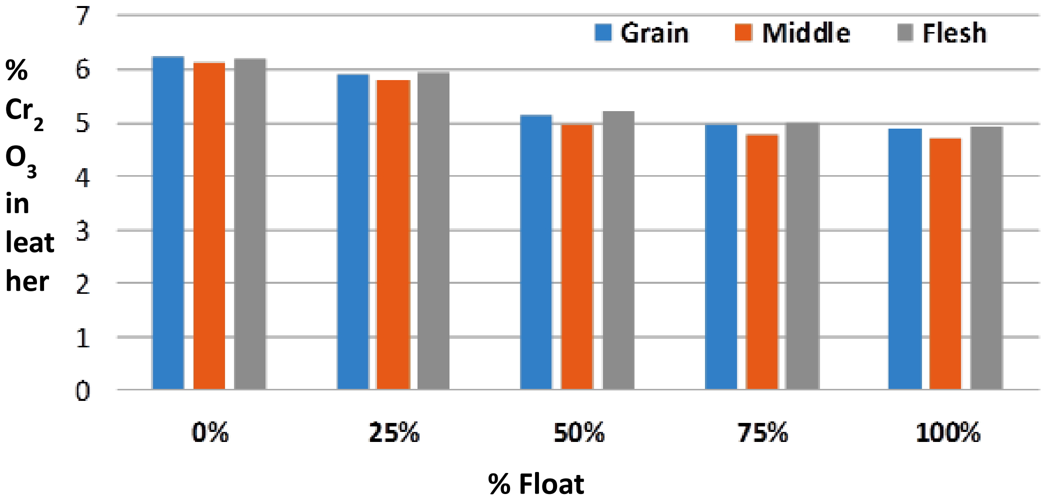


Figure 2. Layer-wise distribution of chromium in wet blue leathers

COMMERCIAL LEVEL VALIDATION OF WATERLESS CHROME TANNING PROCESS

In continuation to the pilot scale trails carried out at CSIR-CLRI, a commercial scale validation of the Waterless Chrome Tanning was planned. With the consent for M/s EKHM tannery, Erode, India, a commercial scale validation was carried out. The raw material was procured from M/s EKHM tannery. The team CSIR-CLRI visited the tannery for carrying out the commercial scale validation of the technology.

Figure 3. Leather experts analyzing the quality of wet-blue leathers

About 1 ton of delimed cow pelt were pre-treated and taken for waterless chrome tanning (0% float and 7% BCS). To enhance the better distribution of chromium, acid stable fatliquor was used prior to addition of BCS. Acid stable fatliquor helps in avoiding acid shock and also immediate fixation of chrome on the surface of the pelts. It also aids in dispersing the chromium molecules from aggregation as well as avoiding the cohesion of the fibers for improved penetration and fixation of chromium during the waterless chrome tanning process. The wet blue leathers made from regular chrome tanning and waterless chrome tanning processes were assessed by the tanners and experts (Figure 3) and the observations are presented in Table 2. The colour of the wet blue was little darker in shade when compared with the conventional wet blue with better fullness. This may be due to the higher offer of BCS and enhanced uptake of chromium in waterless chrome tanning process.

Table 2 Observations on the quality of the wet blue leathers

Parameter	Observations	
	Wet blue from conventional chrome tanning	**Wet blue from Waterless chrome tanning**
Color	Light Blue	Dark Blue
Chrome patches	Nil	Nil
Scud marks	Covered	Covered
Grain smoothness	Good	Good
Uniformity of color	Good	Good
Drawn grain	Nil	Nil
Fullness	Good	Better

The tanners and experts have expressed satisfaction on the overall quality of the wet blue from the trials in comparison to the conventional lot. The tanner was happy to see that such an easy solution exists to solve chrome problem through this technology. He also feels that this technology would form a promising solution for TDS management. The wet blue leathers made from waterless chrome tanning trials were converted in to crust leathers employing regular process. The quality of the crust leathers is comparable to that of the leathers processed by M/s EKHM.

TRANSLATION OF WATERLESS CHROME TANNING TECHNOLOGY IN INDIA AND ABROAD

Figure 4. **Demonstration-cum-workshop at Kanpur leather cluster**

The commercial level demonstration followed by workshop is the strategy followed for the translation of waterless chrome tanning technology to the interested tanners in India. The First demonstration trials at commercial level was launched at Erode, the wet blue hub of India on 5 June 2016, the World Environmental Day to signify the importance of this technology for environmental sustainability. After successful demonstration trials followed by workshop at Erode, Kanpur was chosen as the second cluster for demonstration-cum-workshop. Demonstration of this technology was carried out in three tanneries (Bihari, Homera and Northern tannery) and it was followed by a workshop on 28th July 2016 (Figure 4). Third demonstration was carried out at Jalandhar cluster. Team CLRI visited Jalandhar during 27 August to 1st September 2016 to carryout demonstration and workshop of waterless chrome tanning to the Jalandhar leather cluster. Waterless Chrome Tanning Technology was demonstrated in three tanneries; M/s Paulbro Leathers Pvt. Ltd.; M/s Punjab Hide Co. and M/s Jay Dee Leathers Pvt. Ltd. After successful demonstration, a workshop was held on 31st August 2016 to discuss about technological and commercial aspects of the WLCT process. The processed wetblue leathers from all those demonstrated units were also displayed in the workshop. Team CLRI visited Kolkata during 23rd to 27th October 2016 to carryout fourth demonstration and workshop of waterless chrome tanning to the Kolkata leather cluster. Waterless Chrome Tanning Technology was demonstrated in two tanneries; M/s Zia Hides Pvt Ltd and M/s Indian Tanning Industries Pvt. Ltd at Calcutta Leather Complex (CLC), Kolkata. After successful demonstration, a workshop was held on 27th October 2016 to discuss about technological and commercial aspects of the WLCT process. The processed wetblue leathers from all those demonstrated units were also displayed in the workshop.

So far the technology has been licensed to about 50 tanneries in India. Unique license numbering system was adopted along with license certificate. About 30 commercial level demonstrations with a total of more than 100 tons of drum loads spanning between 1 to 9 tons each of different raw materials such as cow, buffalo, goat and sheep skins were carried out in various clusters as part of demonstrations cum licensing. Brochures were prepared in 3 languages namely English, Hindi and Tamil to meet the needs of the various clusters. A short video was also prepared for workshops.

CSIR-CLRI's "Waterless chrome tanning technology" has now found PAN INDIA acceptance, with tanners in all clusters enrolling for its adoption. This paved way for global reach and several countries including Ethiopia,[16] South Africa, Spain,[17] the Netherlands, Bangladesh,[18] Sri Lanka, New Zealand, Vietnam[19] and Brazil, where several tanners have evinced interest in this technology. Now this technology is making a footing in Ethiopia and further moving forward to other countries of importance.

CONCLUSIONS

Pilot and commercial level studies for developing waterless chrome tanning were conducted. The suitability of the process for the manufacture of different kinds of leathers and the repeatability had been verified. The versatility of the process has also been studied using skins of goat and sheep and hides of Indian cow, buffalo, Ethiopian cow, French cow calf, etc. It was found that the quality of wetblue and finished leathers were on par with the conventionally processed leathers. The roundness was found to be better than the conventional leathers. The process is highly repeatable and yields product of more consistent quality. The process is suitable for all kinds of raw materials. Based on economic, environmental and safety requirements, waterless chrome tanning process appears to be an attractive and practically viable alternative to conventional water mediated chrome tanning process. Further commercialization of this technology in leather industries was attempted through appropriate business plan and joint venture with industrial associations.

ACKNOWLEDGEMENT

Authors thank Mr. Md Hafeel, Managing Partner, M/s EKHM, Erode for providing the raw material and all the facilities to conduct commercial level studies of waterless chrome tanning technology. Authors also wish to thank the financial support from the following projects: Research Initiative for Waterless Tanning (RIWT-CSC0202); Translational research Project (OLP 06) and Fast Track Translational Research Projects (FTT0001MLP)

REFERENCES

1. P. Thanikaivelan, J. R. Rao, B. U. Nair and T. Ramasami, *Crit Rev Env Sci Tec*, 2005, **35**, 37-79.
2. J. R. Rao, M. Kanthimathi, P. Thanikaivelan, K. Sreeram, R. Ramesh, S. Ramalingam, N. Chandrababu, B. Nair and T. Ramasami, *Clean Technol Envir*, 2004, **6**, 243-249.
3. C. Zhang, J. Lin, X. Jia and B. Peng, *J Clean Prod*, DOI: http://dx.doi.org/10.1016/j.jclepro.2015.07.155.
4. J. R. Rao, N. Chandrababu, C. Muralidharan, B. U. Nair, P. Rao and T. Ramasami, *J Clean Prod*, 2003, **11**, 591-599.
5. W. Legesse, P. Thanikaivelan, J. R. Rao and B. U. Nair, *J Am Leather Chem As*, 2002, **97**, 475-486.
6. P. Thanikaivelan, J. R. Rao, B. U. Nair and T. Ramasami, *J Am Leather Chem As*, 2004, **99**, 82-94.
7. V. J. Sundar, C. Muralidharan and A. B. Mandal, *J Clean Prod*, 2013, **59**, 239-244.
8. K. J. Sreeram, S. Ramalingam, J. Raghava Rao, N. K. Chandrababu, B. Unni Nair and T. Ramasami, *Journal of the American Leather Chemists' Association*, 2005, **100**, 257-264.
9. M. Fabbricino, B. Naviglio, G. Tortora and L. d'Antonio, *Journal of Environmental Management*, 2013, **117**, 1-6.
10. G. Ramamurthy, G. Krishnamoorthy, T. Sastry and A. B. Mandal, *Clean Technol Envir*, 2014, **16**, 647-654.

11. R. Manfred, W. Eckhard, J. Björn and G. Helmut, *The Journal of Supercritical Fluids*, 2012, **66**, 291-296.
12. E. Zuriaga-Agustí, M. V. Galiana-Aleixandre, A. Bes-Piá, J. A. Mendoza-Roca, V. Risueño-Puchades and V. Segarra, *J Clean Prod*, 2015, **87**, 874-881.
13. A. Bacardit, S. van der Burgh, J. Armengol and L. Ollé, *J Clean Prod*, 2014, **65**, 568-573.
14. S. Silambarasan, R. Aravindhan, J. R. Rao and P. Thanikaivelan, *Rsc Adv*, 2015, **5**, 66815-66823.
15. R. Aravindhan, P. Thanikaivelan, G.C. Jayakumar, P. Saravanan, J. R. Rao, An improved chrome tanning process, Indian Patent Application No. 201611009091, 2016.
16. R. Aravindhan, P. Thanikaivelan, G.C. Jayakumar, P. Saravanan, J. R. Rao, An improved chrome tanning process, Ethiopia Patent Application No. ET/P/2016/333, 2016.
17. R. Aravindhan, P. Thanikaivelan, G.C. Jayakumar, P. Saravanan, J. R. Rao, An improved chrome tanning process, Spain Patent Application No. 201631104, 2016.
18. R. Aravindhan, P. Thanikaivelan, G.C. Jayakumar, P. Saravanan, J. R. Rao, An improved chrome tanning process, Bangladesh Patent Application No. 197/2016, 2016.
19. R. Aravindhan, P. Thanikaivelan, G.C. Jayakumar, P. Saravanan, J. R. Rao, An improved chrome tanning process, Vietnam Patent Application No. 1-2016-03102, 2016.

SFS O-25

CONCEPT OF SUSTAINABILITY: LOOKING FORWARD

Anne Lama, Jeanette Casey

Institute for Creative Leather Technologies, The University of Northampton, Boughton Green Road, Northampton, NN2 7AL, United Kingdom

**Email: anne.lama@northampton.ac.uk*

The concept of sustainability is not new, dating back to the late 19th Century. Within the leather industry, evidences of growing concern regarding effluent issues were recorded in the late 1800s/early 1900s in various articles published during that period. Introduction of legislations to protect the environment were also seen around the same time. Simple effluent treatment procedures were practiced, as well as various effluent treatment options being investigated. Hexavalent chromium was still in use, however the negative impacts were noted and solutions proposed.

As the leather industry moved to the middle of the 19th Century, focus on effluent treatment increased. Single bath chromium tanning using trivalent chromium was introduced and rapidly became popular, so that in the late 20th Century use of hexavalent chromium was discontinued. The IULTCS (International Union of Leather Technologists and Chemists Societies) effluent commission was formed. The Waste Framework Directive was introduced along with the concept of waste hierarchy. Effluent treatment started to be a standard procedure for many tanneries. The emergence of pressure groups such as ‘environmentalist’ and ‘consumerist’ was also observed during this period.

In the 21st Century, the leather industry has moved beyond simply treating effluent. Focus on certification and authentication has increased. Corporate Social Responsibility has become an integral feature for many organisations. Community and economy are just as important as environment. For a sustainable business strategy it is important to measure the social and financial impact along with the environmental aspect. Therefore, it is becoming critical to adopt the concept of ‘triple bottom line’ and consider all three aspects; social, environmental and economic sustainability, to ensure a sustainable leather industry.

Key words: sustainability, triple bottom line, backcasting

Introduction

Sustainability is now considered a key aspect of modern leather manufacture due to growing concerns about environmental and social welfare.

The concept of sustainability may date back to over 130 years to an idea known as spaceship earth, introduced by economist and philosopher Henry George in his book ‘Progress and poverty’ (Alhaddi

2016; George 2009). This concept over the years saw the emergence of the term “sustainable development” from the Brundtland Report in 1987 (United Nations 1987). The report defined the term as the “development that meets the needs of the present generations without compromising the ability of the future generations to meet their own needs”. The leather industry is and has often been associated with causing environmental pollution in a number of ways: the use of harmful chemicals, water consumption, the generation of large volumes of effluent, end of life disposal and carbon footprinting are still current sustainability issues facing the global industry today.

Late 1800s to early 1900s

Morrison (1911) showed the rising concern regarding pollution within the leather industry, which was certainly not a new phenomenon. The harmful impact of pollution on public health and the environment was recognised. New legislation such as in UK Public Health Act 1875 and River Pollution Prevention Act 1876 was introduced (Bailey 1969).

The leather industry started to react accordingly. A simple treatment option such as filtering tannery effluent before discharge was suggested as a standard procedure (Morrison 1911). Research then followed into a range of treatment options such as precipitation of tanning liquor with lime, biological treatment of sludge using bacteria and purification of liquid tannery waste by oxidation (Morrison 1911). Screening and sedimentation, settling of suspended solids and chemical precipitation was also suggested (Pearse 1915). In addition, good animal husbandry, flaying and preservation practices and process efficiency were mentioned as options to ensure raw material quality in order to reduce wastage. Thoughts were also given to the conversion of waste to energy (Blockey 1915). It is interesting to note that these suggestions are still relevant today.

Although a large number of research articles were published addressing the scientific underpinning of leather technology, the hazardous impacts of certain chemicals were yet to be recognised. For example, arsenic was used during the unhairing processes (Eitner 1907) and the two-bath chromium tanning system with the use of hexavalent chromium was being practiced in the early 1900s. However, the issues of using hexavalent chromium such as development of acute sores in contact with skin wound were noted (Lewin 1908; Bateson 1917). Stomach and kidney diseases among workers were also associated with the application of hexavalent chromium. It was however appreciated that trivalent chromium did not have such hazardous effect (Bateson 1917).

Mid 1900s

According to the literature, the application of hexavalent chromium was limited mainly to the production of glazed or glacé kid leather, but single bath chromium(III) system was becoming popular (Eye 1962; Progress in Leather Science 1920-1945, 1948). This transition was due less to the potential toxicity of hexavalent chromium, but more to fact that the single bath process was more efficient in terms of chromium uptake, the leather did not exhibit any yellowish tone and it allowed reductions in labour and material costs.

The Chemistry and Technology of Leather, Volume III, published by the American Leather Chemists’ Association in 1962, noted that tannery effluent still contained arsenic along with lime, sulfide, fats, greases, salts, surfactants, soluble proteins and solid waste such as flesh, trimmings, hair. However, focus on environmental pollution also increased. Bailey (1969) reported that “public health act 1961 together with the rivers (prevention of pollution) act 1961 the conditions attached to the discharge of trade effluent to sewers and watercourses have become considerably stringent and also costly in most instances".

Analysis of biological oxygen demand (BOD), pH, solids, e.g., total, dissolved, suspended and settleable solids, presence of chlorides, sulfides, nitrogenous compounds and grease were addressed. A number of suggestions, such as monitoring effluent discharge, modification of processes, substitution of hazardous chemicals, recycling, recovery and reuse of usable material in addition of good housekeeping and personnel training (Eye 1962) were suggested, which today would be considered as best practice.

Late 1900s

By the end of 1900s, use of the two-bath chromium tanning system became unthinkable, although mention of alleged practical variations does occasionally still occur. The International Union of Leather Technologists and Chemists Societies (IULTCS) effluent commission was formed and the first meeting was held in September 1970 in Holland (Bailey 1971). The commission discussed the use of low float systems, reuse of water, oxidative unhairing as an alternative to sulfide unhairing, application of enzymes in unhairing, reduction of chemical usage such as lime and vegetable tanning agents to reduce the pollution load. The commission also focused on various options for effluent treatment, such as mechanical treatment or filtration, sedimentation, chemical dosing and biological treatment. These options still form the basis of effluent treatment in the 21st Century.

In 1974, the U.S. Environment Protection Agency produced a guideline titled 'Effluent guideline on pre-treatment standard of leather tanning and finishing' (Environment Protection Agency 1974), and in 1978, a booklet 'Wastes from Tanning, Leather Dressing and Fellmongering' was published by The Department of the Environment in UK (The Department of the Environment 1978) to assist leather manufactures in managing waste and pollution. During this period, The Waste Framework Directive (1975/442/EEC; 1991/156/EEC) (Department for Environment Food & Rural Affairs 2011a) was published, which introduced the concepts of 'the polluter pays' and a 'waste hierarchy'.

The late 1900s also saw the emergence of environmental pressure groups. Sykes (1973) mentioned the impact of the 'environmentalists' and 'consumerists' on the leather industry. He also referred to comments such as: "Chromium is fifty times more toxic than cyanide", in the Sunday Times 5th March 1972, and "We also tested all our samples for arsenic, cadmium and chromium – other poisons" published in Which Magazine of the Consumers' Association January 1973. Sykes (1973) stated that the actions taken by the pressure groups are driven more by emotion than by logic and emphasized the responsibilities of the industry to ensure product quality and performance, as well as responsibilities towards employees and stakeholders.

21st Century

In the 21st Century, technologies have been developed that enable the leather industry to deal with effluent reasonably. Issues with salinity and disposal of solid wastes have remained major concern, but are manageable. Worldwide, regulations have been imposed and adopted to avoid and minimise pollution and the leather industry has reacted accordingly, working towards a 'zero discharge concept'.

The revised Waste Framework Directive 2008/98/EC (Department for Environment Food and Rural Affairs 2011b) introduced the five defined levels of how to manage waste (see Figure 1); prevention must be considered first followed by reuse, recycle, recover and the final option would be disposal. Directive 2000/53/EC (Commission Decision 2005/293/EC), Article 7 specifies that, as of January 2015, 95% of a vehicle required to be reused or recovered and 85% of the vehicle to be reused and recycled based on the vehicle average weight. Perhaps as a consequence, focuses on the wet white technology has increased in order to ease disposal of the end-of-life leather upholstery.

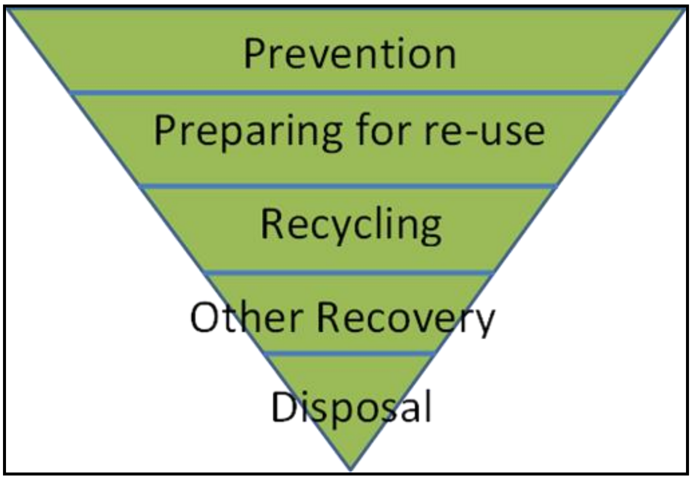


Figure 1. Waste hierarchy model (Department for Environment Food and Rural Affairs 2011b).

Adoption in the leather industry of carbon footprint to measure environmental impact is still a much debated issue: although this calculation may have certain limitations, nevertheless, it remains a major tool to assess product impact. In addition to carbon and water, the TOX footprint, the impact of restricted and harmful substances and resources was suggested by BASF (Wegner and Paczkowski 2014).

One of the key issues that the leather industry may have to face is the end of life product disposal. Global footwear consumption in 2010 was estimated at 20 billion per year (Staikos and Rahimifard 2007). Nowadays, the polluter pays concept is operating: for example electronic appliances, such as mobile phones, computers, televisions etc. can often be returned to the retailers/manufacturers to be recycled or otherwise dealt with. This could mean a similar burden for leather manufacturer.

Various restricted lists have been developed, of which probably the most significant one is the EU's REACH (registration, evaluation, authorisation, and restriction of chemicals) regulation, for defining the application of chemicals to protect consumers, workforce and the environment. The importance of certification (environmental auditing, environmental management certification and eco labelling) became apparent towards the late 20th Century (Sykes 1973), which is now considered one of the key ways of demonstrating that regulations are followed and standards are met.

The rise of pressure groups in the 21st Century, 'environmentalists', 'consumerists' as well as 'animal right' activists, have had a considerable influence on the the international leather industry. Therefore, just focusing of managing environmental pollution is no longer an adequate measure for the survival of the industry. Integrating corporate social responsibility (CSR) as part of the business strategy has become vital, for example the 'Tannery of the Year' not only showcases but celebrates the CSR practices in tanneries.

In 2015, the United Nations launched 'Sustainable development goals - Transforming our World: The 2030 Agenda for Sustainable Development', in which decent work and economic growth is one of the 17 aspects that was featured along with human rights and an environment focus (United Nations 2015). However, people and the environment are also major elements to be considered. True sustainability can only be achieved when all elements are considered simultaneously (Figure 2); hence the triple bottom line (TBL) concept was developed.

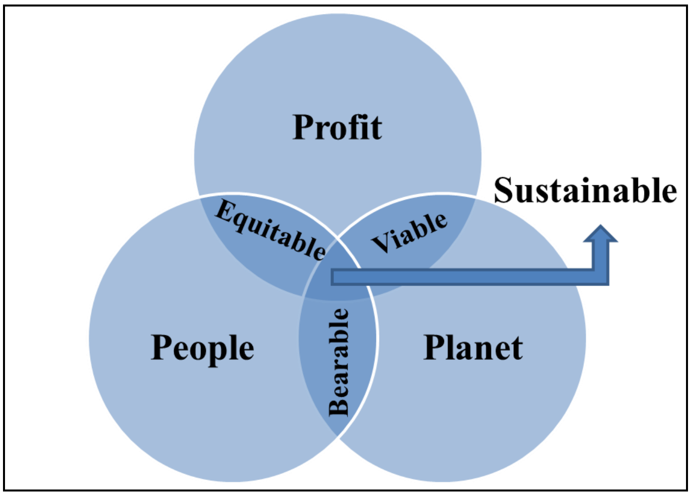
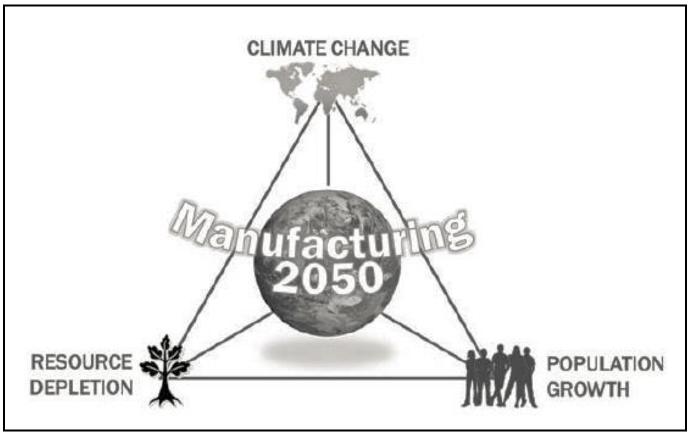


Figure 2: Triple Bottom Line concept illustrating all three aspect of sustainability (adapted from Miller 2015)

In this concept, all three elements, people, profit and environment are given same priority. Progress is evaluated through measuring economic benefit, reduction of negative environmental impact (e.g. reduction of resource consumption and disposal of waste) and social welfare. The environmental and economic benefits are easily measurable, but measuring social benefit can be challenging: nevertheless, TBL is a useful tool to measure the sustainability of an organisation.

United Nations Industrial Development Organization (2003) published a report that demonstrated the influence of triple bottom line on the leather sectors in four Asian countries, India, Pakistan, Sri Lanka and Thailand. This showed that, by adopting the concept, the companies made overall profit, the pollution loading and hence the environmental impact were reduced and the product quality and working conditions were improved, which improved health and safety.

In future, according to Rahimifard et al. (2013) manufacturers will additionally have to consider population growth, depletion of resources and climate change.



Figurers 3: Elements for manufacturers to consider by 2050 (Rahimifard et al. 2013).

Is the leather industry reactive or proactive?

This study showed that the leather industry has always adopted new ideas and concepts and modified them accordingly, whether it has been forced to by the change in legislation, due to pressure groups or because it was simply the right thing to do. However, now and again, it might be beneficial not always to be reactive, but occasionally to be proactive and actually set the goals. The industry as a whole are capable to take the leap to lead leather manufacturing to the future whilst considering the key elements of climate change, population growth and source depletion.

It is common for an organisation to be reactive and make decisions based on forecast and predictions. Conversely, instead of relying on forecasting, Backcasting defined by Quist and Vergragt (2006) as "generating a desirable future, and then looking backwards from that future to the present in order to strategize and to plan how it could be achieved". The theory was proposed in 1970 and have been applied in resource management such as energy (Quist and Vergragt 2006; Giurcoa et al. 2011), water (Sewar, Xu and Turton 2015), development of policy on sustainability (Vergragt and Quist 2011, Paehlke, 2012) and waste management (Head 2015).

The three classic scenario of a strategy development are (Vergragt and Quist 2011);

- What will happen: business as usual scenarios based on trend extrapolations
- What could happen: Strategic scenarios based on forecast, i.e., analysis of past and present data
- What should happen: Normative scenarios based on future vision or desirable futures

Backcasting theory provides a mechanism for setting up future visions or goal that the organisation wants to achieve and then working backwards to set objectives to achieve the final goals (Head 2015). The final vision is shaped by the organisational needs and functions.

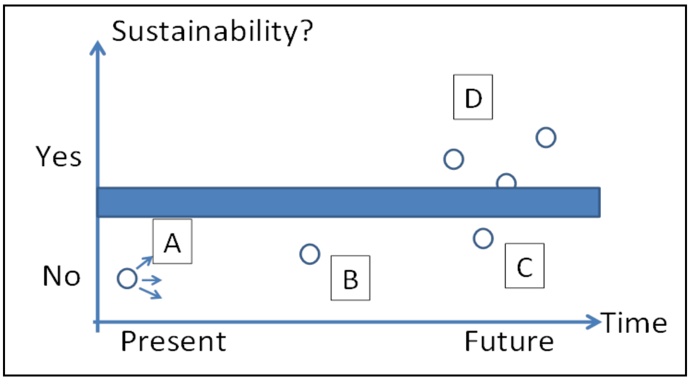


Figure 4: Schematic representation of Backcasting theory; A: directional studies; B: short-term studies to achieve goals; C: forecasting studies and D: other alternatives and visions (adapted from Dreborg 1996).

Transitions towards sustainability require combinations of technological, cultural, social, institutional and organisational changes which can only be implemented through pro-active leadership and the involvement of a broad range of stakeholders, while taking in to account the demand side and the supply chain as related production and consumption systems (Quist and Vergragt 2006). Classical success models of a world that was rather than a world that is developing have often been followed suggesting that leadership is from those who stand, command and protect their followers. The leather industry needs not to settle for classic models but to widen the gap to great leadership. Successful 21st Century leadership has been shaped by environmental change and understanding of the three key aspects of sustainability. The pro-active approach is defined by answering three questions (Torres 2013):

- Where are you looking to anticipate change?
    - Making the decision right now to make a difference rather than reacting because it's mandatory.
- What is the diversity measure of your network?
    - The capacity to develop relationships with people who are different (biological, physical, functional, political, cultural, socio-economic). Despite all differences they trust you enough to work with you to achieve a shared goal. Networks are not just your stakeholders or your company contacts but the workforce, your colleagues, your staff, your employers, your friends and your family.
- Are you courageous enough to abandon the past?
    - Don't reside to keep doing what you've always been doing, dare to be different. People who agree with you are usually those who are different from you yet are willing to join you to take the leap.

The leather industry today has the option to follow business as usual by forecasting based on collective data; or involve a broad range of stakeholders, not only when defining the problem but also when searching for solutions, leaving the past behind to develop visions and goals for a more sustainable future.

Acknowledgement

The authors would like to thank Institute for creative Leather Technologies, The University of Northampton and Prof Anthony D. Covington for supporting this study. The authors also would like to thank to XXXIV International Union of Leather Technologists and Chemists Societies Congress Organisation committee for the opportunity to present the paper at the congress.

References

Alhaddi H, Triple Bottom Line and Sustainability: A Literature Review. Business and Management Studies, 2016, **1**, 6-10.

Bailey D A, A review of the Legislation Affecting the discharge of trade effluent. Journal of the Society of Leather Trades' and Chemists, 1969, **53**, 251-255.

Bailey D A, First meeting of the IULTCS effluent commission Holland 7-9th September 1970, Journal of the Society of Leather Trades' and Chemists, 1971, **55**, 156-157.

Bateson M, The prevention of chrome sores. Journal of the Society of Leather Trades' Chemists, 1917, **1**, 185-186.

Blockey J R, The tannery of fifty years hence? Journal of the American Leather Chemists Association, 1915, **10**, 489-495.

Commission Decision 2005/293/EC of 1 April 2005 laying down detailed rules on the monitoring of the reuse/recovery and reuse/recycling targets set out in Directive 2000/53/EC of the European Parliament and of the Council on end-of-life vehicles (2005) OJ L 94, 13.4.2005, 30-33.

Department for Environment Food & Rural Affairs (DEFRA) The Waste Framework Directive (1975/442, 1991/156 & 2000/60), 2011(a),
Available at http://adlib.everysite.co.uk/adlib/defra/content.aspx?doc=19433&id=19435 (accessed 25 May 2016)

Department for Environment Food & Rural Affairs (DEFRA) Guidance on applying waste hierarchy, 2011(b),
Available at https://www.gov.uk/government/organisations/department-for-environment-food-rural-affairs (accessed 25 May 2016).

Directive 2000/53/EC of the European Parlament and of the council of 18 September 2000, on end-of life vehicles (2005) OJ L 269, 21.10.2000, 34-43

Dreborg K H, Essence of Backcasting, Futures, 1996, **28**, 813-828

Eitner W, On the Action of Arsenic Dehairing, Der Gerber, 779:47 (summary published in Journal of the American Leather Chemists Association, 1907, **2**, 146-147).

Eye J D, The Chemistry and Technology of Leather, Volume III, 1962, Editors: O'Flaherty, F. Roddy, W. T. Lollar, R. M. Robert E. Krieger Publishing Co., Inc. New York, 461-486.

Feairheller S H, John Arthur Wilson memorial lecture on the next major changes in leather manufacturing technology- what is likely to be and how close are we to it? Journal of the American Leather Chemists Association, 1985, **80**, 312-323.

Feikes L, The 1986 John Arthur Wilson Memorial Lecture: leather manufacture and ecology, 1986 Journal of the American Leather Chemists Association, **81**, 234-247.

George H, Progress and poverty, 2009 (Original work published 1879), Cambridge: Cambridge University Press.

Gibson R S and Randall J A, The assessment of chromium status of workers exposed to industrial chromium. Journal of the American Leather Chemists Association, 1987, **82**, 15-21.

Giurcoa D. Cohenb B, Langhama E and Warnkenc M, Backcasting energy futures using industrial ecology, Technological Forecasting and Social Change, 2011, **78**, 797–818.

Lewin, Poisoning by chromium in industrial operations. Ledermarkt, 30 (published in Journal of the American Leather Chemists Association, 1908, **3**:315-316).

Miller R T, Our Triple Bottom Line: It’s Time To Redefine Sustainability, Library Journal, 2015, **140**, 8-9

Morrison J A S, The Treatment of Tannery Effluent. Journal of the American Leather Chemists Association, 1911, **6**, 326-2-343.

Nicholas H, PhD thesis: Development of a Multi-Criteria, GIS-based, Backcasting Framework Model (G-BFM) for Progression Towards Zero Waste Futures, for Holistic Resource Management Policy and Practice in Northamptonshire by 2050, PhD thesis, 2015, The University of Northampton, Northampton.

Paehlke R, Backcasting as a policy tool: the role of values, Critical Policy Studies, 2012, **6**, 337-348.

Panzer C C and Komanowsky M, waste treatment-a guide through maze. Journal of the American Leather Chemists Association, 1985, **80**, 137-149.

Pearse L, Treatment of industrial waste? Journal of the American Leather Chemists Association, 1915, **10**, 293-304.

Progress in Leather Science 1920-1945 Volume III, 1948, British Leather Manufacturers’ Research Association, London.

Quist J and Vergragt P J, Past and future of backcasting: The shift to stakeholder participation and a proposal for a methodological framework, Futures, 2006, **38**, 1027–1045

Rahimifard S, Sheldrick L, Woolley E, Colwill J, Sachidanada M, How to Manufacture a Sustainable Future for Billion People in 2050, “20th CIRP International Conference on Life Cycle Engineering, Singapore, 2013, 1-8.

Sewar P, Xu Y, and Turton, A. Using backcasting to explore ways to improve the national water department’s contribution to good groundwater governance in South Africa, Water International, 2015, **40**, 446-462.

Siegler M, Contribution towards a tanning procedure - free of chrome, Journal of the American Leather Chemists Association, 1987, **82**, 117-124.

Staikos T and Rahimifard S, A Decision-Making Model for Waste Management in the Footwear Industry. International Journal of Production Research, 2007, **45**, 4403-4422.

Sykes R L, A positive approach to the new pressure groups-the consumerists and the environmentalists. Journal of the Society of Leather Technologist and Chemists, 1973, **57**, 123-129.

The Department of the Environment, Wastes from tanning, leather dressing and fellmongering, 1978, London, Her Majesty’s Stationary Office.

Torres R, What it takes to be a great leader. 2013, TED
Available: https://www. ted. com/talks/roselinde_ torres_what_it_takes_to_be_a_great_ leader (accessed 15 December 2016).

U. S. Environment Protection Agency, Effluent guideline on pre-treatment standard of leather tanning and finishing, 1974, (reported in Guidance Manual for Leather Tanning and Finishing Pretreatment Standards, published by EPA, 1984,
Available: https://www3.epa.gov/npdes/pubs/owm0405.pdf (accessed 25 May 2016)

United Nations (UN), Transforming our world: the 2030 agenda for sustainable development, 2013
Available: https://sustainabledevelopment.un.org/?menu=1300 (accessed 25 May 2016)

United Nations Industrial Development Organisations (UNIDO) Triple bottom line demonstration project in four Asian countries, 2015, Vienna Available:https://www.unido.org/fileadmin/user_media/Services/PSD/CSR/Case_studies_-_SE_Asia_TBL_Project.pdf (accessed 14 December 2016) .

United Nations (UN), Our common future - Brundtland report. 1987, Oxford University Press, 204.

Vergragt P J and Quist J, Backcasting for sustainability: Introduction to the special issue, Technological Forecasting & Social Change, 2011, **78**, 747-755.

Wegner B and Paczkowski N, Reducing the Carbon Footprint of Leather, World Leather, 2014, **27**, 34-36.

SFS O -26

THE ELIMINATION OF EFFLUENT FROM LIMING, ACID/SALT PICKLING, AND CHROMIUM TANNING PROCESSES, VERIFIED BY FIVE YEARS HIGH-VOLUME WET BLUE LEATHER MANUFACTURE.

Richard Daniels*, Jiasheng Su, Falei Zhang, Zhuangdou Zhang

Greentech + Associates, Moulton Lane, Boughton, Northampton, NN2 8RF, UK,
E-mail r.daniels@greentech.plus.com
BIOSK, No.6, East Chang Jiang Rd, Development Zone, Shangqui City, Henan Prov, China,
E-mail support@biosk.cn

It is acknowledged that within the chemical processing of hides into leather that the liming, acid pickle and chromium tanning processes are the major contributors of pollutants. This is in terms of biological load, suspended solids, sulfide, nitrogen, chromium, salinity, and the resultant sludges for disposal.

This loading includes unused chemicals that are discharged from these processes due to their poor process efficiencies. Many attempts have been made to lessen this waste at source, but technologies in common use have basically remained unchanged for decades.

Solutions to these problems are far reaching, and the details set down in this paper describe a technology that addresses and resolves these matters. This information was compiled through independent on-site studies within three major tanneries, where approximately 60,000 wet salted US, European and Australian hides per week have been processed since 2013. Accordingly, this paper describes in detail this radical new approach to leather manufacture.

The initial investigations by BIOSK required the building of a full scale wet blue manufacturing plant, and five years of developments before the technology was introduced to industry. The practicality and value of this technology has been since been verified by continuous full scale manufacture by tanners that commenced in 2011.

The technology involves the complete retention and reuse of used floats from liming, pickle and tanning in self-contained loops, and eliminates associated washing cycles. This ensures the complete uptake of processing chemicals, a significant reduction in water use, and zero effluent discharged from these critical manufacturing stages.

1.0 INTRODUCTION

Conventional liming, acid/salt pickling and chrome tanning processes are inefficient in the use of chemicals, and create considerable pollution that has to be addressed within waste water treatment. This effluent is high in biological load, nitrogen, sulfide and suspended solids from the dehairing and liming processes, together with neutral salts and chromium as residual chemicals from tanning. High volume sludge's are also created for disposal.

A five year investigation took place by BIOSK to seek the most effective way to make full use of the chemicals used in process, avoid waste water pollution, and optimise the management of unwanted solids. These objectives were achieved by creating an advanced recycling system – known as BIO-cycle(3) - which resulted in no waste waters being discharged from unhairing/liming, acid/salt pickling and chromium processes. This technology was subsequently introduced to industry in 2011 for full scale manufacture.

The information set down in this paper is based on details provided by independent on-site studies in three major tanneries(1,4) that have since 2013 processed between them 60,000 wet salted USA, European and Australian hides per week

2.0 METHODOLOGY

From initial small scale trials it became clear that the way towards high efficiency liming, pickling and chromium tanning processing would be based on recovering and reusing used floats from processes that remained undiluted by washing cycles. The technology was then developed in a custom built experimental plant fitted with three drums of size 1.8 x 2.2 m diameter for loadings of 40 hides per load, and a series of collection sumps for holding used floats from process.

These findings were refined one year later in a purpose built full scale pilot plant. This included three stainless steel processing drums 5.8 x 6.3 m diameter working with loadings of up to 600 hides /load, two whole hide fleshing machines, and 15 sumps each of size 16 x 3.3 x 2.5 m. These sumps were built into the fabric of the plant during its construction for holding various used floats and wash waters from wet blue manufacture, to optimise their collection, delivery and reuse. See Figure 1:

Figure 1

The BIOSK development plant

Collection sumps for holding the various waste water discharges from wet blue manufacture are shown in the foreground. In tanneries from where the technology has been reported(4), floor mounted holding tanks are used instead of sumps**.**

The technology was considered suitable for use on commercial scale one year later, and it was then offered to industry. This included the three tanneries(4) where information for this paper was sourced in June 2016 that were manufacturing 60,000 hides per week combined at the time of the study. See Table 1:

Table 1:
Tanneries as sources of information(4)

Tannery	**Wet blue production Hides/week**	**Date of commence full-scale manufacture.**
Xing Ning Tannery, Jiang Su Province, China	30,000	2013
Ruisen Leather, Fujian Province, China	18,000	2011
Xinge ye Leather, Fujian Province, China	12,000	2011

The outcome is high-quality high-volume manufacture of chromium tanned hides for sales as wet blue, contract tanning, and in-house processing for finished shoe upper leathers. Central to the system are two self-contained loops:

- A liming recycling process that includes hair recovery
- A pickling and tanning recycling process that includes a combined acid pickle and chrome pretanning stage.

Furthermore, there are no washing cycles following either of these procedures. Both loops rely on the continuous reuse of concentrated used floats that are collected from processes without any dilution with wash waters. Accordingly, due to the absence of washing cycles, there are no residual waste waters for treatment. The technology has been amended by each tannery to suit each individual needs, but details that follow present an accurate summary of the working process.

2.1 The technology for wet blue manufacture from wet salted hides

The processing vessels are conventional wooden drums, loaded with between 450 – 500 wet salted hides. These hides receive a dirt soak, with the used float being discharged. After green fleshing, the hides receive a main soak, with the used float either discharged, or recovered and reused for the dirt soak.

2.1.1 The application of BIO-cycle technology in the liming process

The technology follows these basic steps;

- Undiluted used lime floats that have been filtered, collected and mixed (in a lime-holding tank that serves all of the liming drums) replace the fresh water normally used as float for conventional liming and unhairing
- Chemicals are added for a hair recovery process.

- After two hours the hair is filtered from the float, and the filtered float returned to the liming drum.
- The float is increased using recovered lime liquors from the lime-holding tank, followed by water for controlled osmotic swelling. This can be performed in several additions.
- When the liming process is complete, the float is re-filtered to remove residual hair.
- The load is discharged without any washing, and delivered to a dedicated area for loading onto a line conveyor for feed to the lime fleshing operations. This is followed by lime splitting.
- All of the spillage and drainings from these procedures are collected using dedicated drainage and delivered to the lime-holding tank for reuse in subsequent operations.

There are no washing cycles at the end of the liming process, so the recovered floats remain undiluted. Moreover, they are free of odour and hair residues.

The chemicals offered to the process are conventional - lime, sodium sulfide and sodium hydrosulfide, - although auxiliary products(5) can be included. These additions are at a reduced level when compared to conventional processing due to the presence of unused chemicals that remain in the recovered used liming floats.

2.1.2 The application of BIO-cycle technology in acid/salt pickle and chromium tanning

After lime splitting, the hides are delimed and bated, then drained and washed as conventional practice. The hides may be unloaded from the deliming vessels, then loaded in to the tanning drums. If, however, they are delimed in the tanning drums they must be thoroughly drained before the pickle stage. The technology then follows these basic steps:

A minimum volume of fresh water is added as float for the distribution of salt and acid in the initial pickle stage.

- A small amount of common salt is added, then an acidification using 0.5% formic acid diluted with water.
- Recovered float from previous chromium tanning processes is pumped into the drum at constant rate together with diluted sulfuric acid. This acid has been previously diluted with recovered chrome float.
- The hides are then run for 90 – 120 minutes according the weight range in this simultaneous acid pickle and chrome pre-tannage.
- The main tannage commences with an addition of standard chromium tanning agent, and run for another 4-hours.
- More recovered chromium float is added, then run for a further 4-hours. This includes a basification stage.
- The hides are dumped without any washing, then delivered to a dedicated area for stacking before blue samming.

All of the chromium containing spillage and drainings are collected using dedicated drainage, screened/filtered to remove suspended solids and grease, then delivered to two-holding tank. One tank is for reuse in subsequent acid dilution and for pre-chroming. The second tank is for the offer of chromium that follows the main tannage operations.

3.0 RESULTS AND DISCUSSION

3.1 Managing the technology

There are practical aspects that are required to ensure that this technology works correctly:

The plant must be clean and well managed. All of the pipework and drainage arrangements need to be separate for each stage to avoid any contamination.

The collection tanks are of sufficient size to hold all of the used floats from the processing drums. These tanks are fitted internally with coils for heat exchange, and the temperature adjusted precisely by heat pumps. Typically, the recovered lime floats are adjusted to 22^0C, the recovered chromium float used for pickle and pre-chroming to 22^0C, and the recovered chromium float for tanning to between 55 – 65^0C. These temperatures vary according to the ambient temperature and to accommodate summer winter variations.

This is a hair recovery system, and the hair recovered is very clean, intact, and compact. Being fibrous and clean it is easy to manage and dispose of when compared to contaminated sludge's following conventional effluent treatment. This hair can be composted and has potential to be used in higher value products.

Water is added in the liming process. This makes up the volume balance as it replaces water taken up by the hides in the swelling phase in previous liming cycles. This continuous removal of water together with dissolved neutral salts causes a levelling or a plateau of the salts content in the otherwise closed loop system.

The pickle/tanning system works in a similar way. The hides swell with water from the delimed state to the final chromium tanned condition in previous cycles, and this uptake is replaced by fresh water addition. This continuous water removal enables a levelling of the salts content at a concentration suited to chromium tanning.

3.2 Technical advantages

The technology offers 100% use and uptake of active chemicals. Moreover, the conditions required within the chemical processing do not need to become extreme to achieve a high uptake.

The pH at the end of tanning does not need to be unusually high, the floats very low, or specialised products and control to achieve a chromium uptake that might be good, but always less than 100%. For example, in this situation the final float at the end of tannage is higher than found in many processes and may be as great as 150%. More moderate conditions can prevail through the process.

The leathers produced are clean, have no remaining hair or residues, show no signs of chrome staining, and are relaxed and well extended. They have high commercial value as indicated by the volume of production and the acceptance of this technology in the three major tanneries which form the base for this paper.

Each tannery has adjusted the technology to meet their own individual needs, and so there are no absolute values to judge advantage. However, savings in chemical use and water have been given, and can be expressed as a spread of values across the three tanneries. See Table 2:

Table 2:
Reductions in offers of chemicals and water
(spread of values from three tanneries)

Water / chemicals	**Reduction in chemical offer %** **(on wet salted weight)**
Sodium sulfide + sodium hydrosulfide	0.4 – 1.5
Lime	1.0 – 3.5
Common salt	3.0 – 4.0
Chromium tanning agent	1.0 – 2.5
Water savings	200 – 300 litres/hide

Similarly, the chemical saving as a percentage of the original chemical offers have also been given. See Table 3:

Table 3:
Reductions in chemicals and water based on previous (conventional) processing
(spread of values from three tanneries)

Water / chemicals	**Reduction %** **(on wet salted weight)**
Sodium sulfide + sodium hydrosulfide	18 – 50
Lime	17 - 43
Common salt	57 - 71
Chromium tanning agent	More than 29
Water savings	Up to 50% (excluding saving made by any reuse of used soak floats)

4.0 CONCLUSIONS

A radically different approach to the manufacture of chromium based tannages has been developed. This technology centres on self-contained systems for unhairing/liming and pickle/tanning that ensure that the uptake of processing chemicals in these manufacturing stages is complete.

This approach reduces the offers of active chemicals that are required for processing, eliminates the chemical waste from these process stages, reduces water use, and avoids the treatment of sulfides and chromium from wet blue manufacture. This has not been previously achieved.

The technology requires only the most basic chemicals and equipment although auxiliary products can be included. In manufacture, the focus can remain on making a high quality product and side-step the many technical problems associated with high uptake systems that may be sensitive to control and never 100% efficient.

The technology provides very significant environmental advantages, although these cannot be accurately quantified. This is because each of the tanneries not only manufactures wet blue hides, but continues to process to the finished state. Some of the wet blue are also sold to other tanners or are part of contract tanning. Moreover, process changes have been made since the introduction of this technology to retanning/fatliquoring processes to meet changing customer demands. There were also changes in water consumed to take into account, and although the waste waters from each tannery came from different departments, these waste waters were mixed together for effluent treatment.

However, sulfides are no longer an issue for treatment, and this has resulted in an absence of odour across the effluent treatment plants. There are no chromium based compounds in the waste water from wet blue manufacture, thus avoiding the route of separation, collection, precipitation and possible regeneration.

The biological load is reduced, there is less nitrogen from hair breakdown, and the sodium chloride and TDS content is reduced. The volume of settled solids is significantly reduced, and the management associated with these sludge's and their disposal as waste. The hair that is recovered is very intact, low in moisture and volume, and uncontaminated by products from subsequent processing.

The energy use is also reduced as aeration is no longer need for the removal of sulfide. There are also energy savings for aeration in the biological stage and sludge dewatering. Energy is also saved due to the reduced water requirement and associated temperature controls in manufacture.

Not only does this technology provide environmental advantage, but its commercial viability and value is demonstrated by long-term high-volume leather manufacture of high quality.

Acknowledgements

(1) The site visits and details set down in this paper were performed by R.P. Daniels.
(2) The technology described was fully initiated and developed by BIOSK, China.
(3) The company has more than 10 patents in China, Australia and New Zealand; it is in the process of applying for patents in other countries including the USA.
(4) Thanks to Xing Ning Tannery, Jiang Su Province, China: Ruisen Leather, Fujian Province, China: Xinge ye Leather, Fujian Province, China; for providing complete access to their tanneries at the time of the site visits, and the full provision of information at the time of these visits.
(5) Auxiliaries by BIOSK are available for use within both liming and tanning.
(6) A version of this paper was published in World leather magazine August/September 2016 entitled "A radical new approach within liming and chrome tanning technologies".

PROBIOTIC SOLUTIONS FOR SUSTAINABLE LEATHER

Juan-Carlos Castell*, Claus Reineking

PROVIERA BIOTECH, LLC. 1710 Walnut St. Kansas City, MO 64108 (USA)
STAHL Leinfelden GmbH, Benzstrasse, 11. 70771 Leinfelden-Echterdingen (Germany)

1. INTRODUCTION

Since the introduction of industrial processing in the tanneries only little innovation has taken place. And certainly, most of the new developments were not introduced in the terms of sustainability. Yet, modern times ask for more natural alternatives to the traditional solutions.

Processing hides and skins to manufacture leather involves generating very high amounts of wastewater and solid residues, many of them valuable for other applications if they are not contaminated with chemicals.

For example, 1 tonne of bovine salted hides requires 500 KG of chemicals to produce 250 KG of finished leather (Joint Research Center; Rydin, Stefan; Black, Michael; Scalet, Bianca Maria;, 2013). Therefore, tanners must manage huge excesses of non-leather materials to avoid pollution. When applying R3 environment strategies (European Commission, 2008), main potential actions will focus on:

- Reducing chemicals through efficient methods that optimize dosing and ensure full exhaustion of processing agents and eliminate or improve efficiency of auxiliaries. Consequently, reduction of effluent charges will be expected by improving COD and BOD values, salinity and toxicity.
- Reusing some chemical auxiliaries that remain in the effluents and solid residues that could be applied in the leather process as raw material for, e.g., retanning agents.
- Recycling solid residues by deriving protein, fats and other components to other industries of high value like cosmetics, medicine, food among others. (Adzet Adzet, 2010)

Nowadays, biotechnology is suitable to support tanners to implement R3 environment strategies by reducing the need of synthetic chemicals, improving exhaustion and adding value to by-products. Additionally, technology based on probiotics presented in this work leads to other sustainable benefits, like natural fermentation process, fully renewable raw material, 100% biodegradable, safe biochemicals, reduction of carbon footprint and at the same time improving the quality of the leather articles.

2. TECHNOLOGY FUNDAMENTALS

The word probiotic has been in common use for more than 25 years (Hamilton-Miller, 2003) and definitions have been refined but most describe probiotics as live microorganisms that confer health benefit. Probiotics is on the cutting edge of developing technology to apply the concept of “probiotics” in a variety of industries and applications – from human health, to agriculture, to industrial waste management, textile processing, leather processing, hospitality products and many others. (Proviera.com, 2016)

Probiotics Technology utilizes beneficial and effective microbes to repopulate environments with healthy microorganisms. This work presents the application of the biochemicals in the leather process obtained from a proprietary fermentation and formulation technology. Carefully particular natural raw material is fermented with a probiotic mother culture resulting in metabolites composed by a mixture of biochemicals.

The mother culture is a selection of microbes grown in “consortia”, in a process of co-growth that combines multiple strains during production. Each strain develops while interacting with other. Through the consortia culturing processes, the microorganisms become a small eco system-- much more resilient and capable of working together synergistically. This methodology is more similar to how microorganisms actually survive in the natural environment. In nature, strains never exist in isolation or as a pure culture. Microbes are always interacting with others. (SCD Probiotics, 2016)

Significant differences can be noted when comparing the innovative and disruptive probiotic technology with traditional chemical synthesis:

i. Fermentation is a complete natural bio-reaction and does not require additional sources of external energy. Therefore, carbon footprint is minimized and does not cause greenhouse gas emissions.
ii. Biochemicals derived from fermentation using probiotics do not have potential toxicological effects like synthetic chemicals and are non-corrosive.
iii. Probiotic technology uses raw materials from renewable and sustainable resources and do not depend on other industries like crude oil.
iv. Fermented biochemicals are 100% biodegradable.

Each microbe strain carries specific properties together with its metabolites that enable them to offer functions such as degreasing, dispersing, conditioning etc. These end properties are derived by the cautious use of additives, which are processed using specific manufacturing systems (Proviera.com, 2016).

3. GENERAL PROPERTIES OF PROBIOTIC BIOCHEMICALS

i. Probiotic biochemicals are hydrotropes and possess the ability to increase the solubility of sparingly soluble organic molecules in water (Travis K. Hodgdon, 2007). The biochemicals composition includes some hydrophilic and lipophilic, like typical surfactants, but they contain a very small hydrophobic fraction (Vividha Dhapte, 2015) that does not allow to form aggregates such as micelles. Dirt, dung, waxes, phospholipids among soluble or non-structured proteins, such as hyaluronic acid, dermatan sulfate, elastin, glyco-amino-glycans, globulins, in the hides and skins are cleaved off, solubilized and dispersed into the floats during the first stages of the leather processing, mainly in the soaking operations. Processing chemicals, such as tanning and retanning agents, fatliquors and dyes, are dosed in water solutions to bond the functional groups of the collagen for tanning or to provide all physical properties to the leather articles in the wet-end operations.

   Besides, hydrotropes are recognized as excellent wetting agents when they are in contact with collective structures, such collagen fibers. They allow the media to accept water, working like surfactants, breaking the surface tension of water and help the water transfer from particle to particle (Mark Czernota, 2013). Consequently, water molecules can permeate the fibrous collagen structure into the fibril and micro fibril tissue, up to the α-helix, break hydrogen bonds and activate the protein functional groups. This wetting effect is associated to a slight lyotropic swelling. It produces a relaxation of the fiber structure and allows the fixation of ionic substances. (Ylla-Catala Genís, 2008).

In summary, probiotic biochemicals have strong capabilities to eliminate, or at least to reduce and combine, all kind of soaking and wetting agents, enzymes, degreasers, dispersing agents, solvents, dye auxiliaries, ammonia, extensively used in tanneries in the beamhouse and wet end operation. Most of these agents have high contribution on the effluent pollutants and are not fully biodegradable.

Because they action aims to reduce superficial tension, surfactants require additional washes to be removed from the leather. Potentially, probiotic biochemicals save water consumption as they do not foam.

ii. Probiotic biochemicals are compatible with all chemicals used in the leather making process and do not require to adjust the conditions, such as pH and temperature, beyond those required in the manufacturing operations.

iii. Except under unusual conditions, such as deficient preservation, long soaking, water conditions…, the soaking operation using probiotics biochemicals is free of bactericides and can reduce bad odors or putrefaction. All though the need for bactericides in soaking depends on the totality of all the prevailing conditions (Covington, 2009), they are habitually added in the tanneries. Handling biocides requires adequate safety equipment, increase effluent charges like COD and impact on the efficiency of the biological reactors in the wastewater treatment plants.

Probiotic biochemicals cannot be considered as bactericides, however, they are capable of delaying for a limited time the harmful consequences of certain putrefying bacteria like Bacillus, Staphylococcus spp, Sreptetoccus spp, Klebseilla, E. coli and Listeria, because of bacteria competition exclusion or quorum sensing (Bonnie Bassler, 2006).

4. MATERIAL AND METHODS

This work compiles a set of trials carried out on different materials in industrial drums and pilot plant, from salted to fresh hides from different origins and sheep and goat skins and wet-blue. All demonstrations followed the same processing scheme and the doses and conditions were adjusted as is described below.

Three different probiotic biochemicals (patent pending) have been designed to be differentiated by their hydrophilic-lipophilic-balance (HLB). This was intended to obtain a higher soaking, dispersing or degreasing properties. The products were named as a Probiotic Soaking Agent (PK), Probiotic Dispersing Agent (PS) and Probiotic Degreasing Agent (PD).

Beamhouse:

Wash and presoak:

Objective: Removal of dirty substances from animal (manure, blood…) and preservation substances (salt, biocides…). In salted hides or skins, additional washes are used to reduce salt concentration measured in °Bé. Superficial degreasing to eliminate external waxes and phospholipids on the hair and epidermis.

Dosing: On green weight:

Washes: 0.1% PK and 0% + 0.05% PD. No pH adjustment

Pre-Soak: 0.2% to 0.5% PS, higher in salted raw material + 0% to 0.05% PD. No pH adjustments.

Alternatives to: The probiotic biochemicals replaced surfactants and enzymes (soaking agents) and degreasers. Biocides were not added.

Main soak:

Objective: Re-hydrating hides and skins and bring them to a flaccid condition for subsequent operations. Removal of some globular proteins that will interfere with the tanning process (Thorstensen, 1985).

Dosing: On green weight:

0.3% to 0.5% PK. Higher on fresh raw material + 0% to 0.3% PS.

Products are added prior alkalis to adjust pH=8.5-9.5 for liming.

Alternatives to: Most of the chemical soaking agents, either surfactants or enzymes.

Unhairing/liming:

Objective: Removal of the hair and further completion of globular proteins by the action of the alkali. (Thorstensen, 1985).

Dosing: On green weight:

0.2 % PD, prior to lime and sulfide.

Alternatives to: Eliminate or reduce the use of amines, organic reductive agents and polyphosphates, all of them are typical auxiliaries in the unhairing and liming processes.

Degreasing:

Objectives: Strip off natural fats from adipose tissue, specially inside skins. Disperse natural fats in the float and solubilized them by emulsification with surfactants or hydrolyzation under the action of lipases.

Dosing: Tests were carried out after deliming, before or during the bating for bovine hides, goat skins and sheepskins, or after pickling/depickling for sheepskins. Posterior washes, in most cases, using non-ionic surfactants with high emulsifying effect. Dosages are based on lime pelt weight.

0.5% to 3 % PS + 3% to 6% PD, depending of the natural fat content. Degreasing can need 1 to up to 3 washes.

Alternatives to: Probiotic biochemical can replace and, at least, drastically reduce and have synergies with degreasing agents based on blends of surfactants and lipases. They can replace the need of using solvents as natural fats can be easily stripped off from pelts.

Wet-end:

Objectives: Preservation and conversion of hides and skins into useful commercial article. Achieve resistance to bacterial attack and to high temperatures. Typical tanning methods: mineral (chrome mainly), vegetable and organic (aldehydes, oils, other)

Dosing: On limed pelt weight:
2% to 5% PS
Alternatives to: Dispersing agents and tanning auxiliaries.

Wetting back/washing:

Objectives: Rehydrate tanned leather, wet blue, wet white of vegetable, after a period of piling or storage. To wash leather to obtain regular surface and obtain regular re-hydration. Chelating metallic cations leached from mineral tanning.

Dosing: On shaved weight:
0.5% to 2 % PS, depending on cleanness of tanned leather + 0% to 1 % PK, depending on the dryness + 0% to 1% PG depending on grease content.

Alternatives to: Probiotic biochemical can replace surfactants, ammonia and oxalic acid commonly used to washing and cleaning up wet blue, wet white or vegetable leathers.

Retanning/Fatliquoring/Dyeing:

Objective: Adding and fixing processing chemicals such as retanning agents, fatliquors and dyes, to achieve the final features of the leather articles.

Dosing: On shave weight or double on crust (pearl) weight:
0.5% to 2 % PS or PG

Alternatives to: Surfactants, ammonia and dyes auxiliaries derivate from naphthalene sulfonic and ethoxylated amines.

5. RESULTS AND DISCUSSIONS:

Innovative, all-natural probiotic biochemicals can replace traditional chemicals in the leather tanning industry. Using unique probiotic formulations, the biochemicals are able to improve leather quality, increase yield, lower operating costs and reduce environmental pollution (http://www.provierabiotech.com/, 2016).

Raw hides and skins vary in animal type (bovine, sheep, pig, etc) and across breeds, fat content (prefleshing-mechanical removal of fat from raw hide, different animal types have different levels of natural fat and other characteristics), origin (temperature is the largest indicator for fat content-the colder the more fat, diets vary, species) method of preservation (salted, sun dried, chemical preservatives, raw) as well as cleanliness (raw hides are covered in blood, dung, dirt, etc). Raw hides vary by region. Each of these raw hide characteristics influences the application rate of probiotic biochemicals (Proviera.com, 2016).

In addition to raw hide characteristics each tannery will follow a unique process to produce their desired leather. This includes: brand of chemicals used in each stage, quantity of chemicals used in each stage, process time in each stage, machinery used (drums vs paddles), speed of drum rotations at each stage, water saving methods, mechanical actions, sophistication level of the tannery (fully automated or man power), environmental regulations will vary in each country (sometimes within the same country), hair saving methods or dissolved hair systems, type of tanning (chrome vs vegetable), presence of a wastewater treatment plant, climate, etc. Each of these processing characteristics influences the application rate of probiotic biochemicals (Proviera.com, 2016).

Probiotic biochemicals deliver performance as good as the best of chemicals / enzymes even while offering flexibility in application. They can be applied at wide pH and temperature range. Probiotic biochemicals are compositions, fully biodegradable, non-harmful, safe for tannery workers and leather article consumers. Figure 1 describers each of the products used in the trials and the effects on the leathers.

They can be applied in different stages of the leather making process and general results and benefits are listed below.

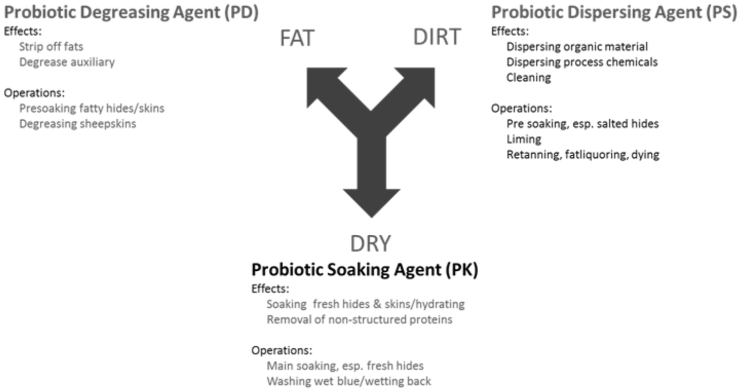


Figure 1: Probiotic biochemical range

Beamhouse:

Wash/presoaking: Avoid putrefaction and bad odors without bactericides. Reduce the soaking time if raw material is very dry. Cleaning and degreasing raw hides/skis surface. Reduction of COD values or increase of BOD/COD ratio. No foaming.

Main soaking: Uniform wetting back. Hides and skins are very clean with slight lyotropic swelling that enhances fiber sponginess and relaxation. Reduction of soaking time when raw hides or skins are dry or became very dry after a long period of storage time. Reduction of COD values or increase of BOD/COD ratio. No foaming.

Typical results of COD analysis of the soaking floats give values ranged between 25 Kg O_2 / tonne of hide to 35 Kg O2 / tonne of hide. With the use of probiotic biochemicals the range was reduced to 15 Kg O2 / tonne of hide to 25 Kg O2 / tonne of hide.

Unhairing/liming: Improve dispersion of lime and open wrinkles. Avoids draw marks and limed pelts are more relaxed and flatter. Easier removal of scud and hair roots. This influences on the up-taking of tanning agents, e.g. higher chromium (III) oxide (Cr_2O_3), and potentially improves quality sorting of leather and increases area yield.

Degreasing: Probiotics biochemicals improve the efficiency of the degreasing proses, even though emulsifiers or lipases must be used in high fatty raw materials. Natural fats impact on the COD and BOD values of the effluent and they can be reduced with probiotics biochemicals. Figure 2 shows the efficiency of degreasing using conventional degreaser agent when 1/3 has been replaced with the same quantity of probiotic degreasing agent (PD).

Tanning: Dispersing of tanning agents to achieve leather more uniform in fullness among different parts, including flanks. Better fixation of tanning agents and potential reduction. Better penetration of tanning agents. Increase of shrinking temperature in wet white leathers.

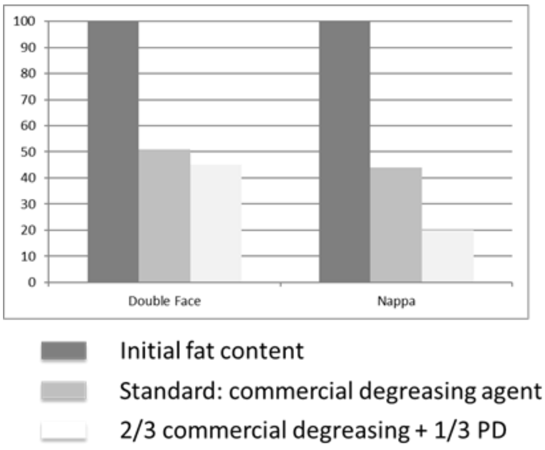


Figure 7: Degreasing efficiency on sheepskins

Wet End:

Washing/wetting back: Clean and uniform surface on the leather. The leather is of a brighter and cleaner appearance than standards. Additionally, probiotics biochemicals do not impact water resistance when manufacturing waterproof articles. No foaming.

Retanning/fatliquoring/dyeing: Better dispersion and exhaustion of leather processing chemicals. Brighter and more uniform colors. Better shade build-up and fault coverage from dyestuffs. Additionally, probiotics biochemicals do not impact water resistance when manufacturing waterproof articles. Potential reduction of nitrogen and sulfates on effluent when probiotic biochemicals replace auxiliaries that highly contribute on these contaminants. Figure 3 compares color intensity and brightness of dyeing using different dye auxiliaries.

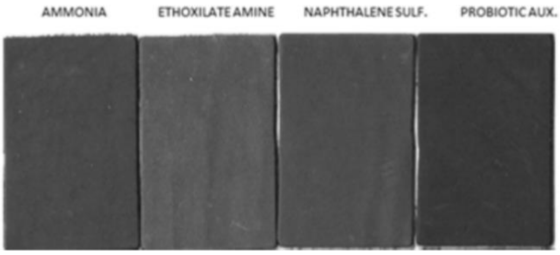


Figure 8: Dye auxiliaries, brightness and intensity

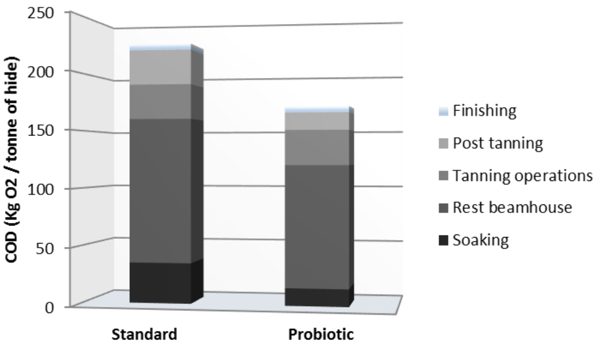


Figure 9: Improvement of COD values

Figure 4 shows the potential COD reduction using probiotic biochemicals. Based on standards, which are widely applied and found generally acceptable (i.e. tends to ignore specific individual situations). Variables that influence the results are the chemicals already used in the tannery, origin of raw hides, preservation methods, mechanical action, etc. (UNIDO, 2016). COD processes with probiotic biochemicals were gathered from trials on wet salted bovine hides with better results. **The potential reduction of COD obtained for the whole process, from wet salted raw bovine hides up to finished leather was up to 24%.**

6. CONCLUSIONS

Probiotics is path breaking technology that enables unmatched processing results across various industries with no impact on environment (Proviera.com, 2016)

Metabolites from proprietary fermentation process of natural ingredients from renewable sources with probiotics are consortia of biochemicals characterized by their hydrotropic properties and capable of delaying the damages caused by bacterial putrefaction, as well as the bad odors produced. Such qualities offer to tanners an exceptional opportunity to replace some chemicals auxiliaries based on chemical synthesis of oil derivate with natural, biodegradable and sustainable alternatives without amending existing manufacturing processes.

The application of probiotic technology to prepare hides and skins for the tanning and the successive operations of leather making improves the quality of the leather articles, save water consumption and costs while reducing environmental impact.

Compared with traditional chemical auxiliaries, probiotic biochemicals are able to transfer water molecules into the smallest interspaces of the fibril collagen structure up to the protein chain, cleave off and disperse substances from hides and skins not suitable to be converted in leather, solubilize organic material and improve the uptake of the reagents that confer final leather properties.

This work demonstrates the potential of the probiotic biochemicals in different stages of the leather manufacture improving the leather quality and reducing effluent pollutants.

7. Acknowledgements

The authors express our appreciation for their support on carrying out this work to:

Dr. S. Pillai and Mr. Ch. Balasubramanian from PROKLEAN TECHNOLOGIES Pvt. Ltd. Plot No: 108&109, Perumal Nagar. Thirumudivakkam, Chenai 600044 (India)
Mr. M. Wood and Dr. N. Tipsrisukond from SCD PROBIOTICS and PROVIERA BIOTECH, 1710 Walnut St. Kansas City, MO 64108 (USA)
All technical WE team from STAHL GROUP.

8. REFERENCES

Adzet Adzet, J. (2010). Transformation of lime splits trimmings into different collagen materials. John Arthur Memorial Lecture. 106th ALCA Annual Meeting.

Bonnie Bassler, L. R. (2006). Bacterially speaking. Bassler Lab Publications, 237-246.

Covington, A. D. (2009). Tanning Chemistry. The Science of Leahter. (T. R. Chemistry, Ed.) Cambridge: Thomas Graham House.

European Commission. (2008). Directive 2008/98/EC. Waste Framework Directive.

Hamilton-Miller, J. (October de 2003). Some insights into the derivation and early uses of the word "probiotic". British Journal of Nutrition, 90(4), pág. 845.

http://www.provierabiotech.com/. (2016).

Joint Research Center; Rydin, Stefan; Black, Michael; Scalet, Bianca Maria;. (2013). BAT Reference Document for the Tanning of Hides and Skins. European Commission.

Mark Czernota, P. T. (2013). Using Surfactants, Wetting Agents and Adjuvants in the Greenhouse. (T. U. Georgia, Ed.) Cooperative Extension(1314).

Proviera.com. (2016). The Probiotic Technology.

SCD Probiotics. (2016). Five Advantages of SCD Pribiotics Technology.

Thorstensen, T. C. (1985). Practical leather technology. Malabar, Florida 32950, USA: Robert E. Krieger Publishing Compnay.

Travis K. Hodgdon, E. W. (June de 2007). Hydrotropic solutions. Current Opinion in Colloid & Interface Science, 12(3), 121-128.

UNIDO. (2016). Pollutants in tannery effluents. .

Vividha Dhapte, P. M. (2015). Advances in hydrotropic solutions: an update review. St. Petersburg Polytechnical University Journal: Physics and Mathematics, 1, 424-435.

Ylla-Catala Genís, A. (2008). La Ribera. Colomer Group.

ECT O-28

CLEAN SALT RECOVERY AND WATER RECYCLING USING NANOFILTRATION AND REVERSE OSMOSIS

Wolfram Scholz

W_2O Environment Ltd., Gymnasiumstr. 6/12, 1180 Vienna, Austria
Email: wolfram@w2oenvironment.net

Tannery wastewater is a complex mixture of organic substances derived from the hide and inorganic substances such as salts and chemicals, which are added during the Beamhouse and Tanyard processing. In tannery effluent high concentration of Sodium Salts such as Sodium Chloride and Sodium Sulphates are found, which remain in the effluent after Primary and Biological treatment, resulting in high Total Dry Solids (TDS) levels after conventional treatment. Consequently many tanneries and leather business parks had to implement Zero Liquid Discharge systems to achieve strict TDS discharge limits, which comprise of a complex Tertiary treatment with Reverse Osmosis and Evaporators. The evaporation of the Reverse Osmosis concentrate shows difficulties, due to the nature and complex mix of residual salts causing scaling, which goes along with difficult disposal of the waste salts.

Nanofiltration membranes retain bi-valent ions and residual organics and leave salty water containing only Sodium Chloride, permeating the membrane. Nanofiltration is operated at a lower pressure of about 8-10 bars, thus consuming less energy than Reverse Osmosis and achieves higher recovery rates of up to 90%. This membrane technology is a suitable pre-treatment, due to the separation of scaling compounds and can improve the performance of Reverse Osmosis and the following Evaporators. The residual salt, after evaporation is pure Sodium Chloride, which can potentially be re-used for salting or pickling.

This combination of Nanofiltration with Reverse Osmosis and Evaporation can improve the overall performance of Tertiary tannery effluent treatment allowing for clean salt recovery and consistent high quality water re-use.

Keywords: Tannery effluent, Nanofiltration, Reverse Osmosis, salt recovery, water recycling

INTRODUCTION

The application of recycling normally relies on suitable process technology for water purification. The wide fluctuation in tannery effluent quality coupled with the requirements for process water of reliable quality tend to favour the application of membrane processes. Membrane filtration processes inevitably play nowadays a key role in modern water recycling since they can produce a water of consistent and reliably high quality. Membranes form a highly selective barrier and are tolerant to shockloads. Therefore the produced permeate quality is varying little with the feed water quality [2]. The main advantage of a membrane based process is that the concentration and separation is achieved without a change of state and without use of chemicals or thermal energy, thus making the process energy efficient and ideally suitable for recycling. [5]

NANOFILTRATION

Nanofiltration (NF) is a pressure drive membrane process, where hydraulic pressure is used to exceed the osmotic pressure of the wastewater, to filter water (permeate) through a semi-permeable Nanofiltration membrane. The residual feed stream (reject) is concentrated up during the filtration process and retains divalent and multivalent ions such as calcium, magnesium, sulphates and metals, which are to large to filter through the membrane.

Picture: 1: Nanofiltration plant installed in France

Nanofiltration technology is suitable for high quality water recycling and re-use for most leather processes, where the recycled process water may contain minor concentrations of Sodiumchloride [6]. The Nanofiltration membrane offers a small pore size of 400 – 600 Dalton, which retains efficiently multivalent ion such as total hardness and certain charged or polar molecules. However, sodium chloride a mono-valent salt, passes the membrane. The spiral-wound modules are densely packed offering a high membrane surface and therefore require only minimum of space. High reductions of COD, BOD and colour are achieved, due to the fact that the Nanofiltration membrane retains organic fractions. The produced permeate is reduced in COD, completely clear and contains minor concentrations of Sodiumchloride. The consistent quality of the NF enables water re-use [4].

Picture: 2: Holding Tank with Nanofiltration permeate for water recycling

Reverse Osmosis

Reverse Osmosis (RO) plants are using a high pressure pump to increase the pressure on the salt side of the RO and force the water across the semi-permeable RO membrane, leaving almost all (around 95% to 99%) of dissolved salts behind in the reject stream. The amount of pressure required depends on the salt concentration of the feed water. The more concentrated the feed water, the more pressure is required to overcome the osmotic pressure.

The desalinated water that is demineralized or deionized, is called permeate (or product) water. The water stream that carries the concentrated contaminants that did not pass through the RO membrane is called the reject (or concentrate) stream.

As the feed water enters the RO membrane under pressure (enough pressure to overcome osmotic pressure) the water molecules pass through the semi-permeable membrane and the salts and other contaminants are not allowed to pass and are discharged through the reject stream (also known as the concentrate or brine stream). The water that makes it through the RO membrane is called permeate or product water and usually has around 95% to 99% of the dissolved salts removed from it.

RO system employs cross-flow filtration, where, the wastewater passes along the membrane filter with the salt-free permeate passing through the membrane and the salt containing concentrate being retained. To avoid build up of contaminants, cross flow filtration allows water to sweep away contaminant build up and also allow enough turbulence to keep the membrane surface clean.

Table 1: Comparison of Nanofiltration and Reverse Osmosis technology

Comparison	Nanofiltration	Reverse Osmosis
Salt retention	Ca^{2+}, SO_4, Cr^{3+}	NaCl
Permeate	NaCl	Salt free
Purpose	Water softening	Desalination
Recovery rate	75 -90 %	65-75%
Operational Pressure	8-12 bars	18-25 bars

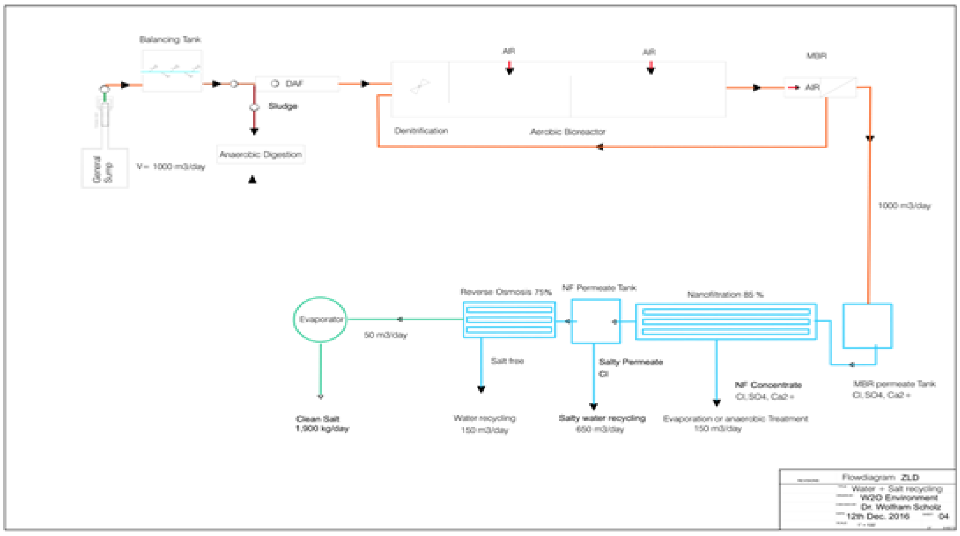
Zero Liquid discharge treatment for tannery CETPs

Many tannery business parks, particularly in India and Tamil Nadu, are operating Zero Liquid Discharge ZDL systems to comply with strict environmental regulations in respect of Total Dissolved Solids, TDS [3]. ZDL effluent treatment systems comprise of Primary and Biological Treatments, using Reverse Osmosis for tertiary Treatment to allow for full water recycling for leather processing. The saline reject derived from Reverse Osmosis is then evaporated in Multiple Effect Evaporators (MEE), with the condensate transferred back for leather processing together with the Reverse Osmosis permeate. The salt residue collected from Evaporation is a mix of mono and multivalent salts, organics and chemicals, which consequently make disposal impossible [1].

The concept of integrating Nanofiltration

A Nanofiltration (NF) plant consists of a pre-pressure pump that transfers the effluents via a cartridge filter to the high-pressure pump. The NF plant has several streets of membrane modules containing 7 membranes each assembled in series and is operated at a pressure between 8-12 bars. Nanofiltration requires less energy than equivalent Reverse Osmosis systems for a similar Feed quality. The slightly salted permeate is collected in a holding tank and can be either recycled back for leather processing or transferred to the following Reverse Osmosis treatment. The plant is fully automatic and shuts down at low level or with changes of the operational pressure. Then the membranes are automatically flushed out with permeate. Compared to Reverse Osmosis higher recovery rates of 75% - 90% can be achieved, which results in a much smaller volume of concentrated brine.

The application of Nanofiltration has shown to completely retain contaminations of larger organic molecules and bi- and multi valent salts, allowing only minor concentrations of Sodium Chloride to filter through the membrane. Nanofiltration treatment is suitable to be integrated into ZLD systems as an ideal pre-treatment before Reverse Osmosis (RO). The slightly salted Permeate contains only Sodium Chloride and can be either re-used for leather processing or diverted for further concentration to the Reverse Osmosis plant. Following Nanofiltration, the performance of the RO plant can improve considerably due to reduced scaling effects, thus achieving higher recovery rates. The concentrate salt brine of the Reverse Osmosis retentate can be evaporated with the multi stage Evaporators achieving a highly clean salt residue, which can be re-used in the tanneries for re-salting or Pickle.



Picture 3: Concept of integration of Nanofiltration into Zero Liquid Discharge treatments

CONCLUSIONS

The integration of Nanofiltration into a ZLD systems can achieve between 75 and 90% of water recovery The high quality permeate, containing only reduced concentrations of Sodium Chloride, can be either re-used for leather processing or be further treated with Reverse Osmosis.

The concentrate of the reverse Osmosis contains only Sodium Chloride, which improves the process of evaporation and reduces scaling of the evaporators. Pure Sodium Chloride salt is achieved, with the following crystallization, which can be re-used for re-salting hides or for Pickle.

Nanofiltration produces a considerably reduced volume of retentate with a significantly lower TDS compared to Reverse Osmosis.

This combination of Nanofiltration and Reverse Osmosis membrane technologies offers a route of treatment and recovery of high quality water and salt at lower treatment costs. Where appropriate, the quantity of recycled water and salt can be carefully managed to achieve a cost-effective recycling solution.

REFERENCES

[1] Aravindhan R., Ramesh R. NK Chandra Babu “Studies on the characterization of the reject stream salt residue and possible reuse in leather Processing”, XXXII Congress of IULTCS May 29th – 31st, 2013 Istanbul, Turkey, p. 138

[2] Judd S. and Bennett A., “Membrane Technology recovers water for industrial reuse”, Industrial water and wastewater treatment, August 2004, P 13-14

[3] Ranipet Tannery Effluent Treatment Co. Ltd., Presentation folder Ranitec

[4] Scholz W.G, Lapoulle A., Cruickshank D., Gigante J.M., “Tannery effluent treatment using Reedbed and Nanofiltration technology”, Leather International, p. 26-28, April, 2007

[5] Scholz W. and Bowden W., “Application of membrane technology in the tanning industry” Leather, 1999, 201 p 17-18

[6] Suthanthararajan R., et.al. “Membrane application for recovery and reuse of water from treated tannery wastewater”, Desalination, 164, 2004 p. 151-156

ECT O-29

TREATMENT OF LEATHER DYES FROM AQUEOUS SOLUTION AND DYE-CONTAINING EFFLUENTS BY NATIVE WHITE-ROT FUNGI STRAINS

Santiago Ortiz-Monsalve*, Mariliz Gutterres, Eduardo Poll, Alan Magalhães and Patrícia Valente

Laboratory for Leather and Environmental Studies (LACOURO), Department of Chemical Engineering, Federal University of Rio Grande do Sul (UFRGS), Av. Luiz Englert s/n°, Porto Alegre-RS, Brazil,
Email: santiago.ortiz@ufrgs.br, mariliz@enq.ufrgs.br
Mycology Laboratory, Department of Microbiology, Immunology and Parasitology, Federal University of Rio Grande do Sul (UFRGS), Rua Sarmento Leite 500 Porto Alegre-RS, Brazil
Email: patricia.valente@ufrgs.br

The discharge of dye-containing effluents in leather production without adequate treatment is a matter of environmental concern. White-rot fungi have been reported for its ability in the treatment of synthetic dyes. This study aimed to investigate the biodecolorization potential and enzymatic activity during the treatment of six leather dyes from aqueous solution by a native fungus collected and isolated in South-Brazil. The strain was identified as Trametes villosa PR-01 based on a molecular analysis of the internal transcribed spacer (ITS) region sequences. The results were compared with data obtained with Trametes sp. SCS-10, previously collected and isolated in a different local and selected for their efficient decolourization ability against different leather dyes. Both strains achieved more than 85% of colour removal of almost all days within 144 h of treatment under submerged fermentation conditions. The increase in the extracellular enzymatic activity laccase (1000–1800 UL^{-1}) was directly linked to the biodecolorization. UV-Vis analyses and tests performed using enzyme inhibitors (NaN_3) suggested enzymatic biodegradation as the mechanism responsible for colour removal. Trametes sp. SCS-10 was tested in different culture conditions to assess its real potential for treatment of dye-containing effluents produced in laboratory scale. The treatment was analysed by means of biodecolorization, laccase activity, TOC and TN removal.

Keywords: White-rot fungi, Trametes villosa, leather dyes, dyeing effluent, biodecolorization,

1. INTRODUCTION

Dyeing is an important step in the production chain of leather, where the sensory characteristics are imparted to the final product. This stage is carried out in the post-tanning operations and is conducted in aqueous medium in drums (Piccin et al. 2012, Piccin et al. 2016). Different chemical compounds such as deacidulants, retanning agents, fat liquoring oils, surfactants, chemical auxiliaries and acids are also added to the wet finishing process to guarantee the desired physical–chemical properties of leather and good exhaustion and fixation of dyes. The composition of the wastewater produced in this step is very variable and depends of various factors such as tanning and dyeing technology applied, type of leather and dye selected (Püntener 2000).

Tannery effluents are characterized by the high biological oxygen demand (BOD), high chemical oxygen demand (COD) and high concentrations of organic carbon and nitrogen (Gutterres et al. 2015). The discharge of dye-containing effluents without adequate treatment is a matter of serious concern by the negative impacts on the environment. Effluents produced in tanneries are usually treated with mechanical, physical-chemical and biological treatments. Wastewaters from wet-ending processes are difficult to treat by conventional methods because of the presence of dyes (Gomes et al. 2016). Advanced technologies such as electrochemical methods (Martinez-Huitle and Brillas 2009), ozonation (Srinivasan et al. 2009), photocatalytic oxidation (Paschoal et al. 2009) and alternative adsorbent materials (Gomes et al. 2016; Piccin et al. 2012), are being widely studied. However, these advanced wastewater treatment techniques are not much used in the leather industry (Gutterres et al. 2008).

Biological strategies are presently earning importance in the treatment of dye-containing wastewaters. White-rot fungi (WRF) have demonstrated ability to remove dyes from wastewater by their highly oxidative, non-specific and non-stereoselective enzyme system. In addition to enzymatic biodegradation, WRF present alternative mechanisms that are involved during dye removal processes, such as biosorption and bioaccumulation (Kaushik and Malik 2009).

Several publications have shown the ability of white-rot fungi to biodegrade/biodecolorize synthetic dyes from aqueous solution; however the treatment of real wastewater is scarcely reported. Previously, Trametes sp. SCS-10 showed great potential for biodecolorization of three leather dyes, due to the mechanisms of enzymatic biodegradation from aqueous solution (Ortiz-Monsalve et al. 2015) and biosorption of leather dyeing from synthetic effluents (Puchana-Rosero et al. 2016).

This study aimed to investigate the biodecolorization potential, enzymatic activity and biomass production during the treatment of six leather dyes from aqueous solution by two native fungal strains collected and isolated in South-Brazil, and the treatment of dye-containing effluents by the previously isolated Trametes sp. SCS-10.

2. MATERIAL AND METHODS

2.1. Fungi and screening

New isolated fungus PR-01 was collected in decayed wood from Farroupilha Park, South Brazil. The strain was identified as Trametes villosa PR-01 based on a molecular analysis of the internal transcribed spacer (ITS) region sequences. T villosa PR-01 was screened among other fungi for its potential to produce ligninolytic enzymes in solid state fermentation, revealed for positive reactions with the indicators ABTS (Jarosz-Wilkołazka et al. 2002) GUA (Kiiskinen et al. 2004) and SYR in three conditions (SYR added alone, SYR + H_2O_2 and SYR + catalase) (Barrasa et al. 2014). Trametes sp. SC-10 was collected and selected in a previous study for their efficient decolourization ability against different leather dyes (Ortiz-Monsalve et al. 2015).

2.2. Media and inoculum

Both strains, PR-01 and SC-10, were maintained on Potato Dextrose Agar (PDA, Difco) at 4 °C. Solid state fermentation was performed in Petri dishes containing 20 mL of Malt Extract Agar (MEA, Merk) supplemented with indicators at 100 mg L^{-1}. Submerged fermentation experiments were performed in 250 mL Erlenmeyer flasks containing 150 mL of Malt Extract Broth (MEB, Merk) and dyes at 200 mgL^{-1}. For inoculum preparation, each strain was grown on MEA plates for 7 days at 30 °C. Agar plugs of growing mycelium (3 mm) were used to inoculum preparations (one disc for solid media and three for liquid media).

2.3. **Dyes and effluents**

Six dyes were provided by Lanxess (São Leopoldo, RS, Brazil): Acid Yellow 79 (AY49), Acid Orange 142 (AO142), Acid Brown 414 (AB414), Acid Red 357 (AR357), Acid Blue 161 (AB161) and Acid Black 210 (AB210), which were used in biodecolorization assays from aqueous solution.

Dyeing effluents were produced in laboratory–scale tannery drums (Mathis LFA model) using a wet-end formulation with the following chemicals for each processing step: (1) Soaking: 200% water, 0.2% formic acid and 0.2% surfactant[1]; (2) Deacidification: 200% water, 1.0% sodium formate, 0.5% sodium bicarbonate and 1.0% neutralizing agent[2], (3) Washing I: 200% water, (4) Fatliquoring, retanning and dyeing I: 100% water, 8% retanning agent[3], 4% vegetable tanning agent[4], 1% dispersing agent[5], 2% dye[6], 6% synthetic oil[7] and 2% formic acid, (5) Washing II: 200% water, (6) Dyeing II: 100% water, 1.5% dye and 1% formic acid and (7) Final washing: 100% water.

[1]Eusapon L-DE®; [2]Sellasol NG®, [3]Basyntan LB-BE®, [4]Weibull Light®, [5]Tamol NA®, [6]**Baygenal Red GT® (Acid Red 357, λ_{max} = 494 nm)** and [7]Lipodermliker LA-SLF® .

The residual waters generated in each step were collected and two wastewaters were composed. Composite wastewater (W1) was obtained by mixing all residual water produced from the steps (1) to (7): soaking to final washing. Composite wastewater W2 was prepared similarly collecting the effluent from the step (2): deacidification to (7) final washing. In this case the wastewater produced in the initial soaking step was not used with the aim of avoid dilution in the dye–containing wastewaters. All wastewaters were stored at 10°C.

2.4. **Biodecolorization assays from aqueous solution**

Dyes (AY49, AO142, AB414, AR357, AB161 and AB210) were added to liquid media and incubated under submerged fermentation conditions. The assays were performed using the active mycelial pellets of T. villosa PR-01 and Trametes sp. SCS-10 growing in dye-containing media as described above. Dye AR357 was selected to obtain kinetics of biodecolorization with both strains in the presence of the enzyme inhibitor sodium azide (0.1 mM). Biodecolorization was determined by UV-Vis spectral analysis in a range between 400–800 nm, and was expressed in terms of biodecolorization efficiency:$BE\ (\%) = \frac{A_o - A_t}{A_o} \times 100$, A_o and A_t represent the initial and observed absorbance post-treatment, respectively, at the λ_{Max} of each dye.

2.5. **Biodecolorization assays from dye-containing effluents**

The assays of decolourization of the effluents were performed assessing two different conditions of addition of carbon and nitrogen sources. In the first conditions (N1) the composition of the medium MEB was emulated: 2% (m/v) of malt extract and 1% (m/v) of glucose. In the second condition (N2) the concentration of nutrients was reduced at 50% (1% of malt extract and 0.5% of glucose). These nutrients were aseptically added to the wastewaters (W1 and W2). All wastewater were inoculated as described earlier and incubated under submerged fermentation conditions (30 °C and 200 rpm for 15 days). Biodecolorization was measured as indicated above.

2.6. **Analytical procedures**

To study the kinetics of biodecolorization related to colour removal and enzyme activity, samples were withdrawn from the liquid cultures or effluent every 24 h, centrifuged and micro-filtrated. The supernatant was used to measure biodecolorization and laccase enzyme activity. Extracellular Lac activity was determined by monitoring the oxidation of ABTS at 405 nm ($\varepsilon 405 = 3.6 \times 104\ M^{-1}\ cm^{-1}$) for 5 min. The reaction consisted of an aliquot of enzyme extract added to ABTS solution containing 1 mM ABTS in 0.2 M sodium acetate buffer (pH 4.5) (Wang and Ng 2006). Wastewater compositions were characterized before and after the treatment by fungi. Samples were analysed by pH, total organic carbon (TOC) and total nitrogen (TN). TOC and TN were assessed in a TOC/TN-L analyser (Shimadzu SSM- 5000A, Japan).

3. RESULTS AND DISCUSSION

3.1. **Isolation and screening of leather dye biodecolorization by fungi**

From six fungal strains isolated and assessed for the ability to produce ligninolytic enzymes and decolorize leather dyes in solid media, the strain PR-01 showed activity in the medium with guaiacol and ABTS, revealed by the formation of coloured zones around microbial growth (Fig. 1). These reactions with the indicator substrates suggested the activity of extracellular oxidases (Jarosz-Wilkołazka et al. 2002; Kiiskinen et al. 2004). Laccase activity was confirmed by the positive reaction with SYR in presence of catalase and in absence of H_2O_2 (Barrasa et al. 2014). Additionally, PR-01 showed the best results for decolorization of all six dyes assessed in solid media. These results are similar to those obtained with the reference strain Trametes sp. SCS-10 (Tab. 1).

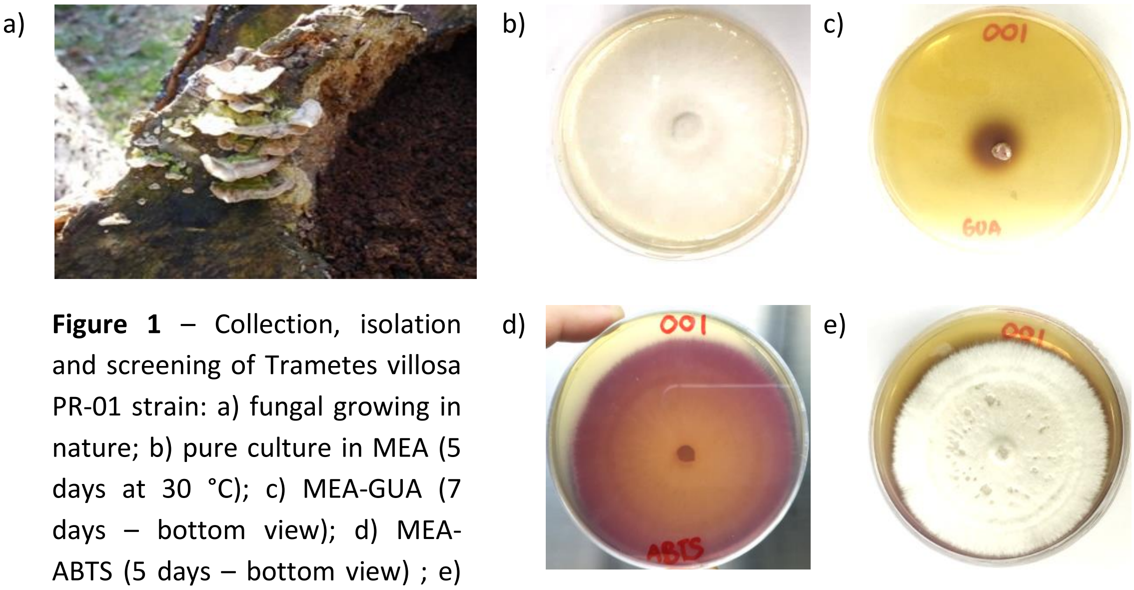


Figure 1 – Collection, isolation and screening of Trametes villosa PR-01 strain: a) fungal growing in nature; b) pure culture in MEA (5 days at 30 °C); c) MEA-GUA (7 days – bottom view); d) MEA-ABTS (5 days – bottom view) ; e) MEA-SYR (5 days – bottom view).

Table 1 –Screening of native fungi to produce ligninolytic enzymes and to biodecolorize leather dyes in solid media.

Strain	Agar plate screening for ligninolytic enzyme production					Agar plate screening for dye biodecolorization					
	GUA	ABTS	SYR[a]	SYR[b]	SYR[c]	AY79	AO142	AB414	AR357	AB210	AB161
T. villosa PR-01	+	+	++	+	+	++	+	++	+	+	+
Trametes sp. SCS-10	+	+	++	+	+	+	+	+	++	+	++

(+) Positive test; (−) Negative test; (++) Better qualitative reaction as compared to control strain;

[a] Reaction with indicator substrate added alone; [b] Reaction with indicator substrate SYR in the presence of catalase; [c] Reaction with SYR in the presence of hydrogen peroxide (H_2O_2).

3.2. **Biodecolorization of leather dyes from aqueous solution**

Two white rot fungi, newly isolated T. villosa PR-01 and previously isolated Trametes sp. SCS-10, were used to biodecolorize six leather dyes while growing in dye-containing media. Both strains showed potential to grow and biodecolorize all six leather dyes assessed in different rate and extent (Fig. 2). T. villosa PR-01 showed the best results for the dyes AB161 and AR357, achieving 89.44 ± 2.78 and 85.71 ± 1.20 % of colour removal, respectively. However, Trametes sp. SCS-10 achieved higher values of biodecolorization for the same dyes, 91.43 ± 0.47% for AB161 and 91.43 ± 0.47 for AR357, confirming previously results presented by Ortiz-Monsalve et al. (2015). Similarly, AO142 decolourization was approximately 80% by Trametes sp. SCS-10 and just 60% by Trametes villosa PR-01. Instead, PR-01 strain showed better results than SCS-10 in the colour removal of AB414, AB210 and AY79. The different efficiency of biodecolorization of each strain in the same conditions of treatment is related with the difference in the structure of dyes. The fungal metabolisms are affected by the presence of functional groups linked to dye molecule such as aromatic compounds, heavy metals, salts and chromophores functional groups. The presence of these agents may also cause changes in pH and inhibit both mycelial growth and production of ligninolytic enzymes associated with biodegradation, reducing the dye removal efficiency (Kaushik and Malik 2009; Ali 2010). The different results obtained with both strains demonstrate the importance to continue searching for native strains with ability to treat a wide range of industrial dyes. Some qualitative results are shown in Figure 3.

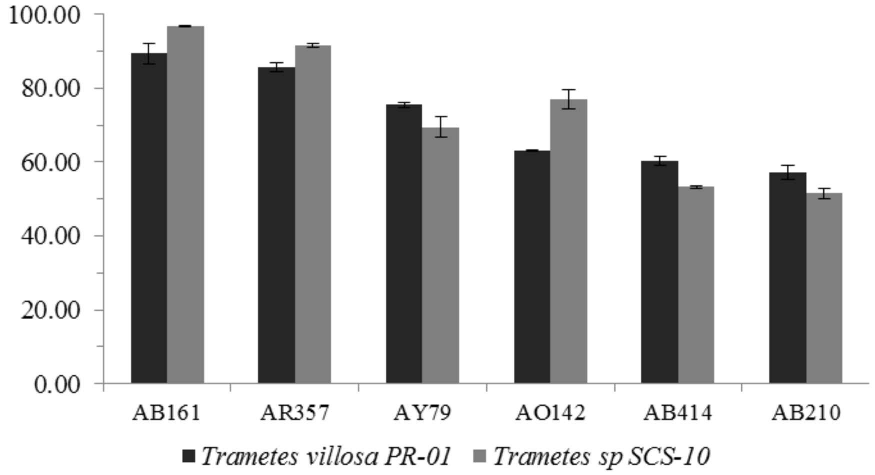


Figure 2 – Biodecolorization of different leather dyes from aqueous solution by native strains of Trametes villosa PR-01 and Trametes sp. SCS-10: AB161 (Acid Blue 161), AR357 (Acid Red 357), AY79 (Acid Yellow 79), AO142 (Acid Orange 142), AB414 (Acid Brown 414) and AB210 (Acid Black 210).

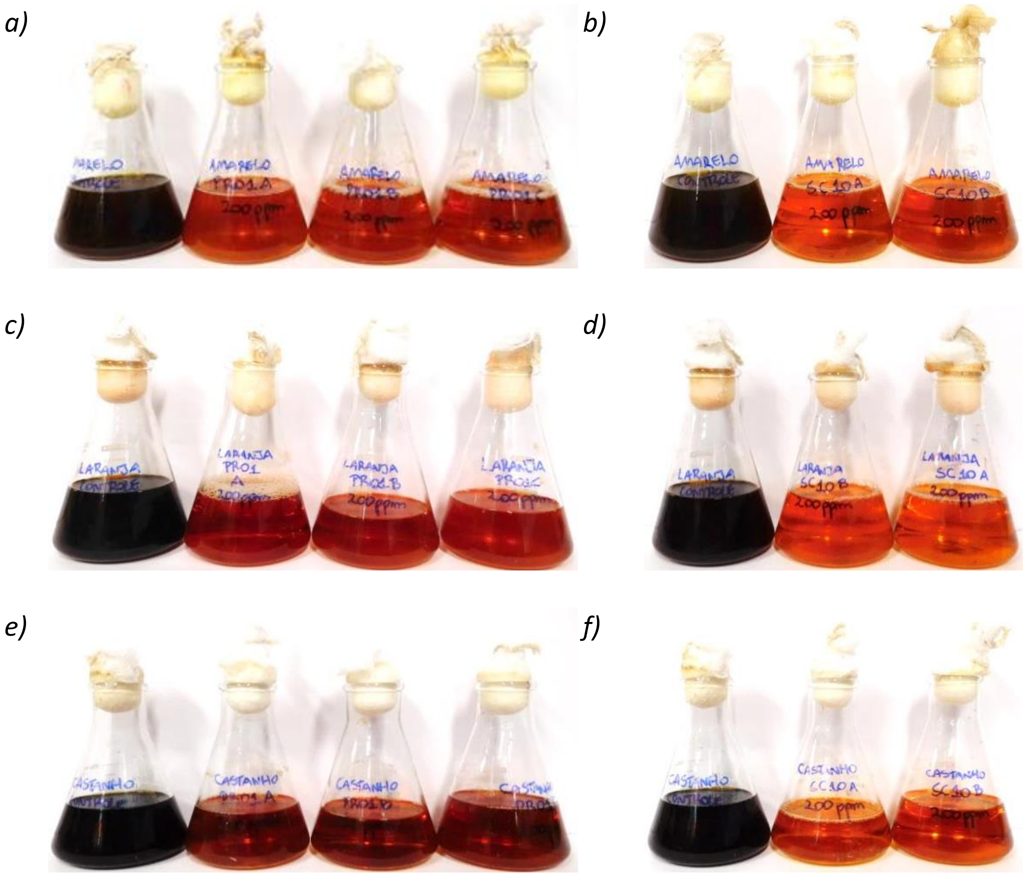


Figure 3 – Biodecolorization of leather dyes by a native isolate of *Trametes villosa* PR-01: *a)* Acid Yellow 79; *c)* Acid Orange 142; *e)* Acid Brown 414 and *Trametes* sp. SCS-10: *b)* AY79; *d)* AO142; *f)* AB414. All photos were taken after 8 day of incubation in MEB broth at 30 °C and 200 rpm. The Erlenmeyer at left of each photo represents the abiotic control for each dye.

Trametes villosa PR-01 and Trametes sp. SCS-10 showed high efficiency of biodecolorization of AR357 dye. This leather dye was selected to study the kinetics of biodecolorization, related to colour removal and enzyme activity with both strains (Fig. 4). In Figure 4a is shown how the greatest performance of Trametes sp. SCS-10 was correlated with the activity of laccase. The strain achieved 15% of colour removal in the first 48 h of treatment; however, after 96 h it increased above 90%. In this period (72 – 96 h), Lac showed the higher levels of activity (1,636.85 ±32.30 UL−1). Similarly, Trametes villosa PR-01 reached the maximum rate of biodecolorization within 96 h, the period when Lac activity increased to 1,299.26 ± 47.52 UL^{-1} (Fig. 4b). The involvement of laccase as mechanism of biodecolorization was studied in a test performed using enzyme inhibitors. Laccases of both strains were inhibited about 98 – 100 % by NaN_3 at 0.1 mM (Fig. 4a–b). These enzymatic inhibitions lead to values of colour removal of 15 and 10% with Trametes sp. SCS-10 and T. villosa PR-01, respectively. The colour removal observed in presence of inhibitor or when enzymatic activity was not detected in the first 24–48 h of treatment without inhibitors is related to a mechanism of dye adsorption by the fungal mycelium (biosorption). Similar results were reported in other species of Trametes, which colour removal where related to biomass adsorption and biodegradation, such as T. versicolor in the removal of Gryfalan Black RL metal complex dye (Aksu and Karabayır 2008) and T. trogii in biodecolorization of commercial anthraquinonic and azo dyes (Park et al. 2007).

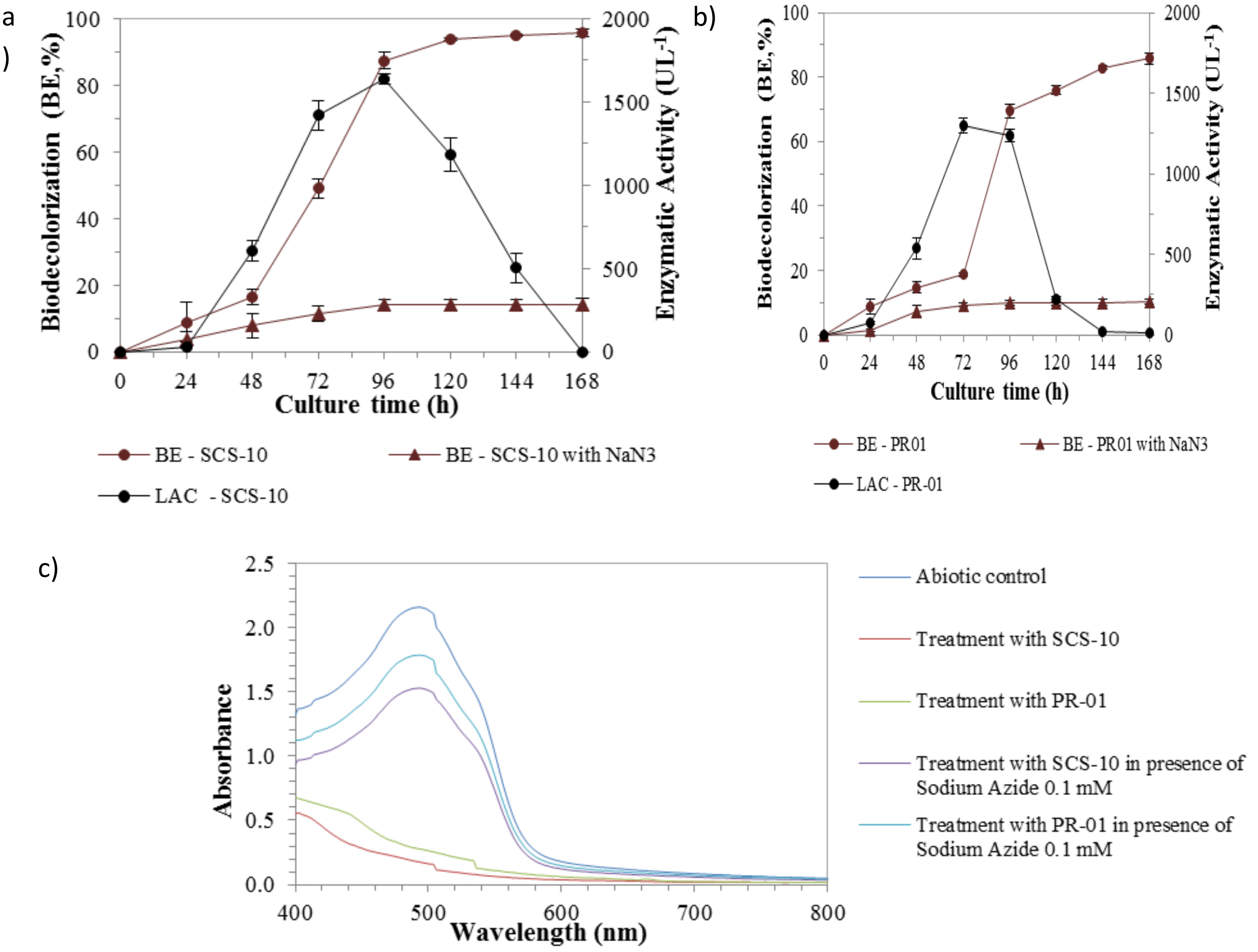


Figure 4 – Biodecolorization kinetics of AR357 by a native strain of a) Trametes sp. SCS-10; b) Trametes villosa PR-01; c) UV-Visible spectrum analysis during biodecolorization of leather dyes by SCS-10 and PR-01 strains in presence/absence of enzymatic inhibitor NaN_3.

3.3. **Treatment of leather dyeing wastewater**

Trametes sp. SCS-10 was selected for its great potential to biodecolorize six leather dyes from aqueous solution to treat leather dyeing effluents. The fungus showed also ability to biodecolorize all wastewaters tested, achieving over 90% of colour removal in all conditions tested (Table 3). In the decolourization profile of the wastewaters (Fig. 6a) is shown a similar behaviour to that observed in the kinetics of decolourization of AR357 from aqueous solution; the maximum biodecolorization efficiency was correlated with the highest activity of laccase. An initial mechanism of biosorption was observed in the first period (24–96 hours) of treatment. However, this step was followed by a mechanism of enzymatic biodegradation and the mycelium preserves its original colour after treatment. When the conditions of concentration of nutrients were tested, a slightly improvement in biodecolorization was observed. For example, in the case of wastewater W1, the increase in the concentration of nutrient sources lead from 95.38 ± 0.31± 1.01% (N2) to 97.58 ± 1.06% (N1) of colour removal. Similar results were obtained for W2, when the increase in nutrients conditions lead from 92.57± 0.66% (N2) to 94.65 ± 0.31% (N1) of decolourization. However, laccase activity was not affected and peaks of activity were observed between 1500–1800 UL^{-1} for both treatment conditions. This may explain why the variation in the nutrient concentration did not show significant influence ($p \leq 0.05$) on the biodecolorization efficiency, under the conditions assessed. Figure 5b shows the profile of biodecolorization of wastewater W1, displaying the relation with the increment of Lac activity. UV-Vis spectrum analysis showed changes in the peak patterns. All wastewater conditions showed the same characteristic peak at 494 nm of AR357. In Figure 5b is showed how the characteristic peak of W2 wastewater disappeared completely within 168 h in both treatments N1 and N2.

Decrease in TOC and TN was also observed after biodecolorization of the composite wastewaters. Above 80% of reduction of TOC was observed in both treatments N1 and N2. Although reduction of TN was not so expressive. This efficiency in the reduction of total organic carbons suggested the disrupting reactions of dye molecules and other chemical compounds present in wastewater into simpler fragments. Similar results were reported by Asgher et al. (2014) in the treatment of textile effluents by crude ligninolytic enzymes extract from Schyzohyllum commune IBL-06. Rosales et al. (2011) also found a reduction in TOC when compared the efficiencies of the decolourization of leather dyes by enzymatic and electrochemical treatments. However, authors reported just 23% of TOC reduction by the commercial laccase from Trametes versicolor. Similarly, Novotný et al. (2011) studied the colour removal and TOC reduction of dyes from aqueous solution based on the enzymatic degradation by fungi Irpex lacteus followed by anaerobic degradation in bacterial reactors. Authors reported TOC reduction with fungi treatment; however the second step using bacteria was more efficient in TOC removal. According with authors, an additional treatment is necessary to complete the TOC removal from wastewater, since fungi can initiate the degradation of recalcitrant compounds, however are not able to achieve complete mineralization (Hai et al. 2008). Therefore, the treatment of dye containing wastewaters may be enhanced using microbial consortium consisting of both fungi and bacteria may be efficient in biodegradation and mineralization of synthetic dyes and other organic xenobiotics (Ali 2010). The pH values during the process of decolourization were cosntant during the tratment in a range of (4.5–6.0). However was observed that in the treatment of wastwewater W1 were obtained slightly higher values of efficiency of decolourization and lac activity. pH of W1 wastewater varied between 4.5–5.0. This pH value is close to the optimum for laccase activity. treatment of dyeing effluent, since it usually has an alkaline character (Rodríguez-Couto, 2015). Previoulsy, Trametes sp. SCS-10 showed high biodecolorization and Lac activity in a wide pH range (4.0–7.0) (Ortiz–Monsalve et al. 2015). Similar behaviours were reported in other strains of the genus Trametes: T. maxima at pH 6.0 (Hernández-Luna et al. 2008) and T. trogii at pH 6.0–11 (Yesilada et al. 2002). Although the increase in the concentration of dyes and other xenobiotic compounds as salts and surfactants have been reported as inhibitors of the capacity of white rot-fungi to treat wastwewaters, no significant difference was found in the treatment with Trametes sp. SCS-10 of the W1 and W2 composite wastewaters under the conditions tested .

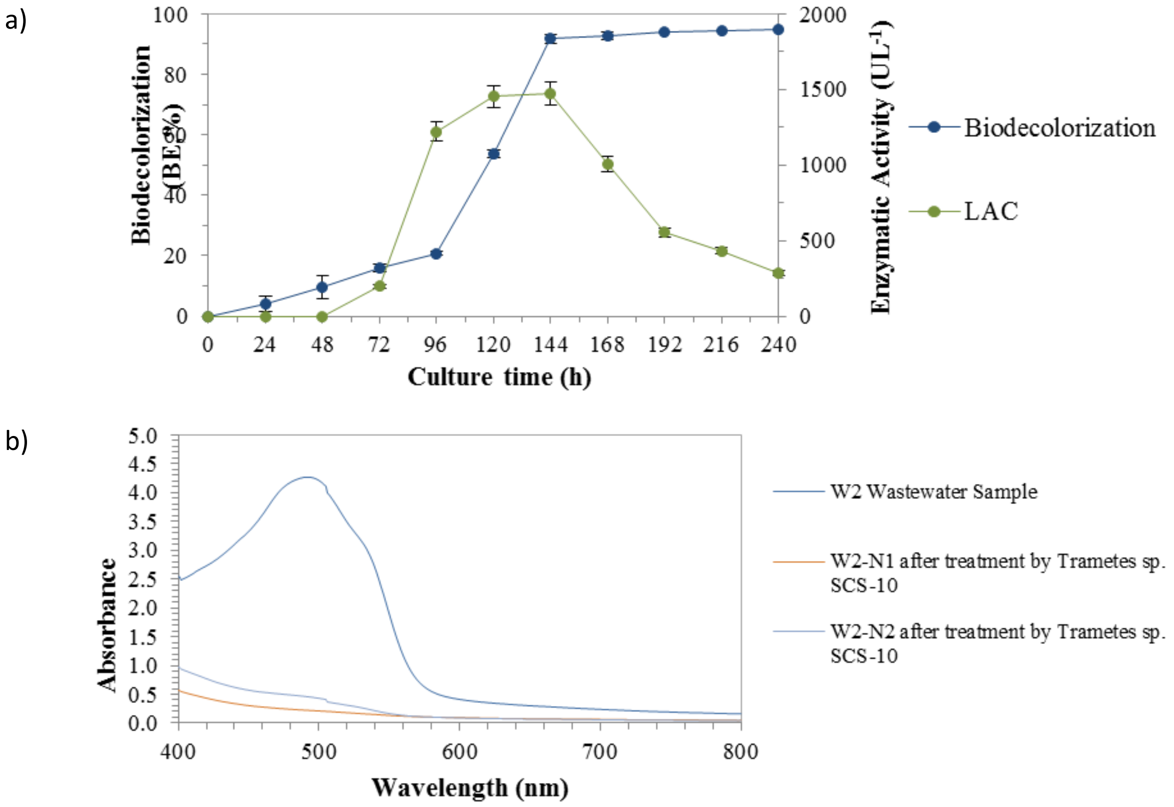


Figure 5 – a) Biodecolorization kinetics of leather dyeing wastewater (W2–N1 and W2–N2) by a native strain of Trametes sp. SCS-10; b) UV-Visible spectrum analysis during biodecolorization

Table 2 – Biodecolorization, Laccase activity, TOC and TN removal during treatment of dye-containing effluents by Trametes sp. SCS-10

CompositeWastewater	BE[a] (%)	Lac[b] (UL^{-1}) – Time (h)[c]	TOC($mg\ L^{-1}$)[d]			TN ($mg\ L^{-1}$)[e]		
			Before treatment	After treatment	Removal (%)	Before treatment	After treatment	Removal (%)
W1 – N1	97.58 ± 1.06	1731.48 ± 88.38 – 144	2150.01	334.12	84.46	27.44	23.60	13.96
W1 – N2	95.38 ± 0.31	1775.52 ± 12.83 – 168		285.25	86.73		19.01	30.72
W2 – N1	94.65 ± 0.31	1562.96 ± 79.80 – 144	1886.50	212.61	88.73	26.35	17.87	32.20
W2 – N2	92.57± 0.66	1628.96 ± 195.04 – 168		262.97	86.06		20.33	22.83

[a] Biodecolorization efficiency after 10 days of treatment; [b] Laccase activity peak during treatment; [c] Time of maximum peak of Lac activity; [d,] Total organic carbon (TOC); [e] Total nitrogen (TN).

4. CONCLUSION

The new isolated strain of Trametes Villosa PR-01 showed activity of extracellular oxidases and laccase activity and good decolourization for all six dyes (AY49, AO142, AB414, AR357, AB161 and AB210) assessed in solid media. These results were similar to those obtained with the reference strain Trametes sp. SCS-10. In aqueous solution comparing the dyes, T. villosa PR-01 showed high biodecolorization efficiency for AB161 and AR357, achieving 89.44 ± 2.78 and 85.71 ± 1.20 % of colour removal, respectively. However, Trametes sp. SCS-10 achieved higher values of colour removal for the same dyes, 91.43 ± 0.47% for AB161 and 91.43 ± 0.47 for AR357. In the study of the kinetics of biodecolorization of AR357 dye the strains of Trametes sp. SCS-10 and Trametes villosa PR-01 achieved above 90% of colour removal after 96 h when Lac activity showed peaks of activity (1,636.85 ±32.30 UL^{-1} and 1,299.26 ± 47.52 UL UL^{-1}), respectively. The fungus Trametes sp. SCS-10 also showed ability to biodecolorize the dyeing wastewaters tested, achieving over 90% of colour removal and above 80% of TOC reduction for all assays, with two composed wastewaters each one with different conditions of carbon addition and nitrogen sources.

5. ACKNOWLEDGEMENTS

The authors are grateful to the Funding for Studies and Projects (FINEP, Brazil) for the financial support in the Public Call CTHIDRO–Hydric Resources Management, to the Administrative Department of Science, Technology and Innovation (COLCIENCIAS, Colombia) for financial support and scholarships and to the Business Leather Unit of LANXESS Company for the technical support.

6. REFERENCES

- Aksu Z, Karabayır G, Comparison of biosorption properties of different kinds of fungi for the removal of Gryfalan Black RL metal-complex dye. Bioresour. Technol. 2008, 99, 7730–7741.
- Ali H, Biodegradation of Synthetic Dyes: A Review. Water, Air, Soil Pollut. 2010, 213, 251–273.
- Asgher M, Yasmeen Q, Iqbal H M N, Development of novel enzymatic bioremediation process for textile industry effluents through response surface methodology. Ecol. Eng. 2014, 63, 1–11.
- Barrasa J M, Blanco M N, Esteve-Raventós F, Altés Alberto, Checa Julia, Martínez A T, Ruiz-Dueñas F J, Wood and humus decay strategies by white-rot basidiomycetes correlate with two different dye decolorization and enzyme secretion patterns on agar plates. Fungal Genet. Biol. 2014, 72, 106–14.
- Gomes C S, Piccin J S, Gutterres M, Optimizing adsorption parameters in tannery-dye-containing effluent treatment with leather shaving waste. Process Saf. Environ. Prot. 2016, 99, 98–106.
- Gutterres M, Fontoura J, Benvenuti J, Ortiz-Monsalve S, Characterization of RawWastewater fromTanneries. J. Soc. Leather, Technol. and Chem. 2015, 99, 280–287.
- Gutterres M, Passos J, Aquim P, Severo L, Trierweiler J, Reduction of water demand and treatment cost in tanneries through reuse technique. J. Am. Leather Chem. Assoc. 2007, 103, 138–143.
- Hai F I, Yamamoto K, Nakajima F, Fukushi K, Removal of structurally different dyes in submerged membrane fungi reactor-biosorption/PAC-adsorption, membrane retention and biodegradation. Journal of Membrane Science. 2008, 325, 395–403.
- Hernández-Luna C E, Gutiérrez-Soto G, Salcedo-Martínez S M, Screening for decolorizing basidiomycetes in Mexico. World J. Microbiol. Biotechnol. 2008, 24, 465–473.
- Jarosz-Wilkołazka A, Kochmańska-Rdest J, Malarcžyk E, Wardas W, Leonowicz A, Fungi and their ability to decolourize azo and anthraquinonic dyes. Enzyme Microb. Technol. 2002, 30, 566–572.

- Kaushik P, Malik A., Fungal dye decolourization: recent advances and future potential. Environ. Int. 2009, 35, 127–141.
- Kiiskinen L L, Rättö M, Kruus K, Screening for novel laccase-producing microbes. J. Appl. Microbiol. 2004, 97, 640–646.
- Martinez-Huitle CA, Brillas E, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review. Appl. Catal. B. 2009, 87, 105–145.
- Novotný C, Svobodová K, Benada O, Kofroňová O, Heissenberger A, Fuchs W, Potential of combined fungal and bacterial treatment for color removal in textile wastewater. Bioresour. Technol. 2011, 102, 879–888.
- Ortiz-Monsalve S et al., Decolorization of leather dyes by a native isolate of Trametes sp. SC10. XXXIII IULTCS Congress, ABQTIC, 2015, 1–10
- Park C, Lee M, Lee B, Kim S, Chase H, Lee J, Kim S, Biodegradation and biosorption for decolorization of synthetic dyes by Funalia trogii. Biochem. Eng. J. 2007, 36, 59–65.
- Paschoal F M M, Anderson M A, Zanoni M V B, Simultaneous removal of chromium and leather dye from simulated tannery effluent by photoelectrochemistry. Appl. Catal., B. 2009, 166, 531–537.
- Piccin J S, Gomes C S, Mella B, Gutterres M, Color removal from real leather dyeing effluent using tannery waste as an adsorbent. J. Environ. Chem. Eng. 2016, 4, 1061–1067.
- Piccin J S, Gomes C S, Feris L, Gutterres M, Kinetics and isotherms of leather dye adsorption by tannery solid waste. Chem. Eng. J. 2012, 183, 30–38.
- Puchana-Rosero M J, Lima E, Ortiz-Monsalve S, Mella B, da Costa D, Poll E, Gutterres M, Fungal biomass as biosorbent for the removal of Acid Blue 161 dye in aqueous solution. Environ. Sci. Pollut. Res. 2016, 1–10.
- Püntener A G., Leather Dyes. In Freeman H S and Peters A T, eds., Colorants for Non-Textile Applications; Elsevier Science. Amsterdam, 2000, pp. 478–484.
- Rosales E, Pazos M, Sanromán M A, Comparative efficiencies of the decolourisation of leather dyes by enzymatic and electrochemical treatments. Desalination, 2011, 278, 312–317.
- Srinivasan S V, Rema T, Chitra K, Sri Balakameswari K, Suthanthararajan R, Uma M B, Rajamani S.Decolourisation of leather dye by ozonation. Desalination. 2009, 235, 88–92.
- Wang H X, Ng T B, Purification of a laccase from fruiting bodies of the mushroom Pleurotus eryngii. Appl. Microbiol. Biotechnol. 2006, 69, 521–525.
- Yesilada O, Cing S, Asma D, Decolourisation of the textile dye Astrazon Red FBL by Funalia trogii pellets. Bioresour. Technol. 2002, 81, 155–157.

ECT O-30

NOVEL FORMALDEHYDE SCAVENGER CONTAINING ACTIVE METHYLENE FOR THE EFFICIENTLY REMOVAL OF FORMALDEHYDE IN LEATHER

Ting Zhang*, Xuechuan Wang, Longfang Ren

College of Bioresources Chemical and Materials Engineering, Shaanxi University of Science and Technology, 710021, China
Email: wangxc@sust.edu.cn

As a kind of harmful substances, formaldehyde has some effect in induced carcinoma and promoted cancer process. Formaldehyde is a common chemical feedstock for numerous of industrial processes, it also used for the product of resin, rubber, coating, adhesive, etc. In leather technology, formaldehyde used as preservative, biocide and it also a raw material of amino resin and synthetic tanning agent. In order to meet the increasingly stringent formaldehyde evaluation standard, many approaches have been widely developed for eliminating formaldehyde. Chemical reaction is one of the most effective measures for scavenging formaldehyde in a certain short period. Formaldehyde eliminated by its high chemical reactivity, but most of the reactions belong to reversible reaction, easy to cause secondary pollution.

Methylene hydrogen of α-hydrogen containing compound type which has high activity can react with formaldehyde at normal temperature. Above all, this reaction is irresistible. According to this mechanism, a hyperbranched polymer containing active methylene (HAMP) was designed through transesterification reaction. The characteristics of hyperbranched polymer which has high functionality of terminal group cause its excellent reactivity, the unique structure of hyperbranched polymer can clear formaldehyde by physical adsorption for the molecular cavity.

The structure of HAMP was characterized by fourier transform infrared(FTIR), nuclear magnetic resonance(NMR), gel permeation chromatography(GPC) and dynamic light scattering(DLS). Formaldehyde-removal capacity of HAMP has been investigated in leather retanning process. The results indicated that the optimum amount of HAMP was 4wt% and the reaction time was 2h. Removal rate achieved 88.4%, formaldehyde content of leather disposed by HAMP was lower than 180mg/kg. Meanwhile, the treated leather has been investigated by scanning electron microscope from that we can see collagen fibers became looser. Physical-mechanical property had slightly changes. Tensile strength changed from 8.31 N/mm^2 to 8.17N/mm^2 and tearing strength reduced to 22.57 N/mm from 29.54 N/mm, softness achieved 8.5.

Key words: formaldehyde scavenger, active methylene, leather

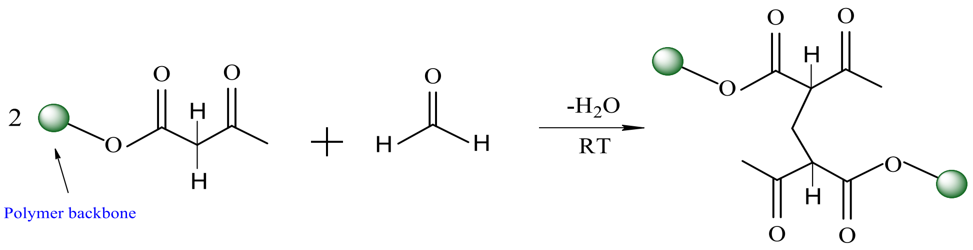
1. INTRODUCTION

Formaldehyde (HCHO), one of the most typical volatile organic compounds (VOCs), plays an important role in the chemical production due to its high chemical reactivity[1-3]. HCHO is a common chemical feedstock for numerous of industrial processes, it also is used as the raw material of resin, rubber, coating, adhesive, etc[4]. In leather manufacturing process, HCHO mainly is used as preservative, biocide and the raw material of amino resin and synthetic tanning agent. As far as the HCHO of leather is concerned, its use as a component of tanning agent is of special significance.

Discussion about HCHO as a possible carcinogen starts from 1980 when the influence of HCHO on mice was reported. HCHO is identified as class 1 carcinogen in 2004 by World Health Organization (WHO), it has some effect on induced carcinoma and promoted cancer process[5]. Low concentration of HCHO can easily result in respiratory disease after long-term inhalation exposure. Human immunity begins to decline at high concentration due to the crosslinking and solidification of HCHO and protein molecules and it is probable to result in the nucleus gene mutations, DNA protein crosslinking and DNA crosslinking with a single bond[6-7]. Therefore, it is urgent to develop practical and effective approaches to eliminate HCHO.

In order to meet the increasingly stringent HCHO evaluation standard, many approaches have been widely developed for eliminating HCHO, including physical adsorption[8], chemical reaction[9], absorption by using plant[10], biological filtration[11], photocatalytic oxidation[12] and plasma purification[13-14]. However, HCHO removal is still a challenging problem due to different restrictions. Physical adsorption method easily causes secondary pollution, photocatalytic oxidation is invalid at night for the lack of ultraviolet and the equipment of plasma purification is expensive [15-17]. These applications were hard to apply to actual situation due to its low efficiency and high energy consumption [18]. Chemical reaction is one of the most effective measures for scavenging HCHO in a certain short period. HCHO can be eliminated by its high chemical reactivity, but most of the reactions belong to reversible reaction, as a result, it is easy to cause secondary pollution.

Methylene hydrogen of α-hydrogen containing compound type which has high activity can react with HCHO at normal temperature (Scheme 1). Above all, this reaction is irresistible [19-20]. According to this mechanism, a hyperbranched polymer containing active methylene was designed through transesterification reaction. The characteristic of hyperbranched polymer which has high functionality of terminal group is excellent reactivity, as well as the unique structure of hyperbranched polymer can scavenge HCHO by physical adsorption for the molecular cavity. Beyond that, leather softness improved when the polymer as a kind of adsorption material is applied in the leather process.



Scheme 1 Reaction mechanism for condensation of hyperbranched polymer with acetoacetyl group and formaldehyde

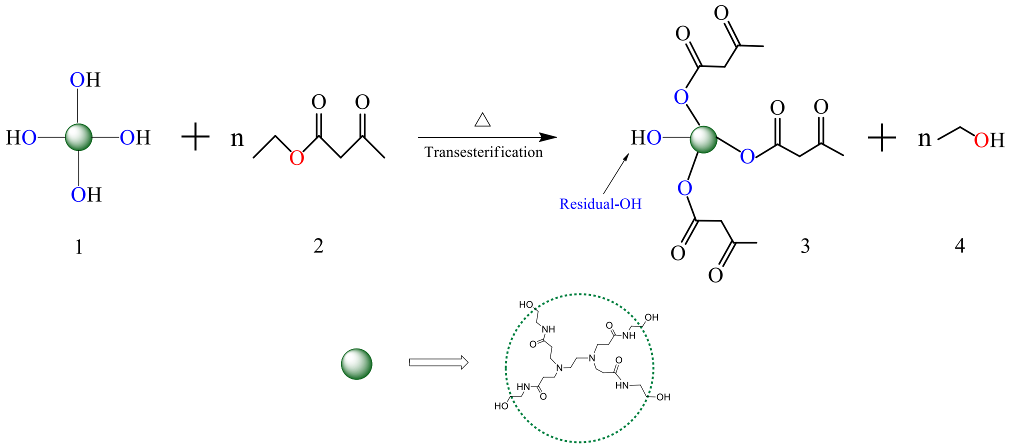
2. EXPERIMENTAL

2.1. Materials

Sheep skin was supplied by Hebei Dongming Leather Co., Ltd. Ethyl acetoacetate ($C_6H_{10}O_3$) and acetyl acetone ($C_5H_8O_2$) were provided by Tianjin Kermel Chemical Reagent Co., Ltd. Formaldehyde solution (HCHO) and anhydrous potassium carbonate (K_2CO_3) were purchased from Tianjin Baishi Chemical Co., Ltd. The hydroxyl-terminated hyperbranched polymer ($C_{22}H_{44}N_6O_8$) was purchased from Weihai CY Dendrimer Technology Company. All the reagents based on the above were of analytical grade and used without purification. Meanwhile deionized water was used in this experiment.

2.2. Synthesis of the formaldehyde scavenger

Ethyl acetoacetate (2) and K_2CO_3 were added to a three-neck flask equipped with a stirring rod, a separatory funnel and a set of distillation device. K_2CO_3 played a role of catalyst in the reaction. Rising temperature to 100°C after reactants fully mixed together. Hydroxyl-terminated hyperbranched polymer (1) was added into above flask throught separatory funnel, and this temperature was kept for 5 hours until this reaction completely finished. The dosage of HBP and EAA was n(HBP):n(EAA)=1:2, catalyst was wt. 2% (basing on the total mass of reactants). The unreacted EAA in the reaction mixture was removed by rotary evaporation instrument, and the further purification was carried out by using acetone. Finally, the hyperbranched polymer containing active methylene (3HAMP) was obtained according to the transesterification reaction (Sheme 2), the product was yellow and viscous.



Scheme 2. Synthesis route of the formalydehyde scavenger

2.3. Characterization

Gel permeation chromatography (GPC) was obtained on a Waters 2695 GPC system with polyethylene glycol as standard sample, mobile phase was $NaNO_3$ with a flow rate of 1.0mL/min.

Fourier transform infrared (FTIR) spectra were recorded with VECTOR-22 spectrometer within the range of 4000–400 cm^{-1} by using KBr as carrier to fix the samples.

Nuclear magnetic resonance (NMR) analyses were measured using the ADVANCEⅢ 400MHz spectrometer with deuterium oxide (D_2O) as solvents.

The samples was dissolved in water to form a solution with the concentration of lg/L, the Dynamic light scattering (DLS) measurements were performed on an instrument (Zetasizer NANO-ZS90),

2.4. Removal capacity of HCHO

First of all, the preparation of HCHO standard curve is required[21]. The formaldehyde solutions with different concentration gradient were prepared by diluting wt. 37% formaldehyde solution. 5 mL formaldehyde solution and the same amount of acetyl acetone were added in a test tube, and then it was heated to about 90℃ for 5min (distilled water was as blank reagent). The testing sample was cooled down in the dark for 30min at room temperature. Absorbance of the mixture solution was measured in 412 nm wavelength of visible spectrophotometer. The formaldehyde content in solution was calculated by HCHO standard curve.

Test the HCHO concentration in this system before and after HAMP was added. The calculation of formaldehyde removal rate was carried out via following equation.

$$W = \frac{W_1 - W_2}{W_1} \times 100\%$$

Where W is the removal rate of formaldehyde (%); $W_1$and W_2 are the initial and final HCHO concentration in the solution (mg/mL), respectively.

2.5. Removal procedure of formaldehyde in leather

Sheep skin, dicyandiamide resin retanning agent, and HAMP were used in the retanning experiment. Extraction method of the formaldehyde in leather is on the basis of GB/T 2912.2-2009. The removal procedure are shown in Table 1**.**

Table 1 Retanning process of goatskin garment leather

Process	Amount/%	Chemicals	Time/min	Temperature/℃	pH	Remark
backwater	200	water		40		
	1.5	degreaser（DE SOAGEN DN）	40			
	0.5	formic acid	20		3.8	
washing	200	water	10	40		
chromium retanning	100	water		40		
	3	Tankrom FS	120			
	0.5~1	sodium bicarbonate	2*30+60		3.8~4.1	
overnight						
neutralization	100	water		40		
	2.0	neutralizer (DESOTAN NT)				
	1	sodium bicarbonate	2*20+30		5.5~5.8	Examination incision
washing	200	water	10	40		
retanning	100	water		40		

	6	retanning agent (DESOATEN A-17)	60			
washing	200	water	10	40		
dyeing and fatliquoring	100	water		50		
	8	DESOTAN SO	60			
	1	DESOSTAR BLACK-FN	30			Dissolution with water
	1	formic acid	30		3.5-4	
removal formaldehyde	200	water				
	X	HAMP	n	50		Tested the formaldehyde content

3. RESULTS AND DISCUSSION

3.1. Characterization of HAMP

Tab. 2 presents the molecular weights and polydispersity indexes (PDI) of HBP and HAMP by GPC. As a kind of spherical polymer, the relationship between relative molecular mass of HBP with radius of fluid mechanics or with the rotation radius was different from with that of linear molecules. Therefore, molecular weight determined by polyethylene glycol was smaller than predetermined molecular weight[22]. The results indicated that the transesterification reaction was successful. PDI is 1.07 and 1.15, which indicated the molecular weight distribution was uniform.

Table 2 GPC characteristics of HBP and HAMP

Sample	Mn	Mw	PDI	Predetermined molecular weight
HBP	330	374	1.07	521
HAMP	464	535	1.15	689

As shown in Fig.1a, the peaks at 3300 cm^{-1} belong to –OH, which confirmed a high hydroxyl concentration in HBP. The absorption bands in the region of 1000-1200 cm^{-1} are assigned to the C-O stretching vibrations in hydroxyl groups. The peak around 1641 cm^{-1} is ascribed to the C=O stretching vibrations in amide groups. The band at 1551 cm^{-1} is indicative of the N-H bending vibration in amide groups[23]. Compared with Fig.1a, a new peak centered in the range of 1745～1725cm^{-1} which belongs to the vibration of ester group (-O-CO-) appears. In addition, the peak at 3286 cm^{-1} in HAMP polymer becomes weaker because many hydroxyl groups have reacted with ester groups, which indicates transesterification reaction is carried out according to the expected route.

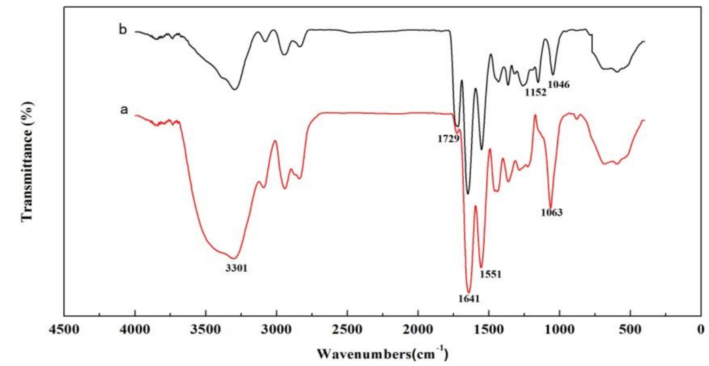


Fig.1. FTIR spectra of HBP (a) and HAMP (b)

Fig.2 shows the ^{1}H-NMR spectra of HBP (A) and HAMP (B). As shown in Fig.2, the signal at 4.79ppm belongs to the solvent peak. In Fig.2A the signals at 2.37ppm (a) and 3.65ppm (b) correlating to the asymmetric two absorption peaks of the H in the methylene connected with nitrogen. The signals at 2.50ppm (c) related to -CO-CH$_2$- proton, 8.03ppm (d) is for the -CO-NH- proton. In addition, the peaks at 2.7~3.7ppm (e、f、b) belonge to the -CH$_2$- protons connected with -NCO, the protons linked with -OH in HBP are observed at 3.65ppm. In Fig.2B, the signals at 2.88ppm (h) is for –CO-CH$_2$-CO- proton and 2.25ppm (i) is for -CO-CH$_3$ proton in HAMP. The peaks at 4.21ppm (g) is assigned to the –CH$_2$-O-CO- protons in HBP. Compared with Fig.2A, new signals appears at g, h, I, which confirms that the transesterification reaction had been successfully conducted. However, in fact, hydroxyl group can not be completely replaced by acetoacetyl group, which is shown in Fig.2B.

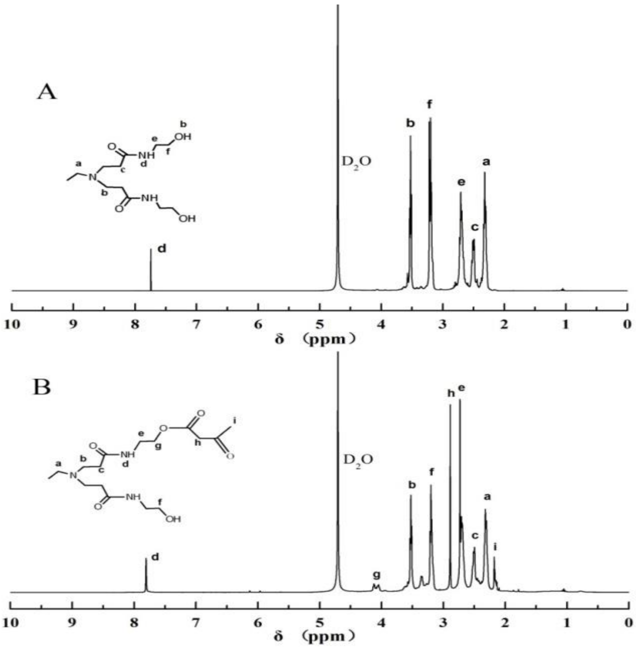


Fig.2 ^{1}H-NMR spectra of HBP (A) and HAMP (B)

DLS measurements were performed to evaluate the particle size distribution of HAMP. From Fig.3, we could see that the peak was narrow and pointed, which indicated that the size distribution of HAMP was uniform. The average particle size was 0.37μm, which also indicated the stability of the product was excellent.

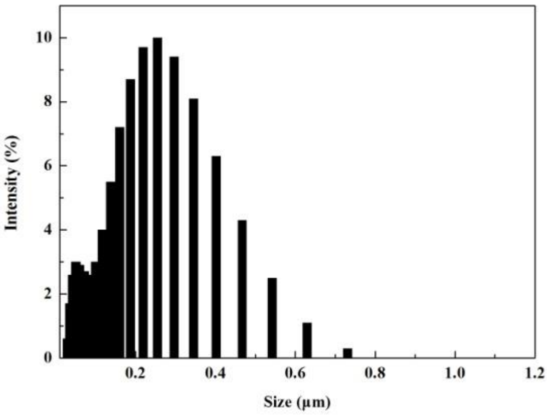
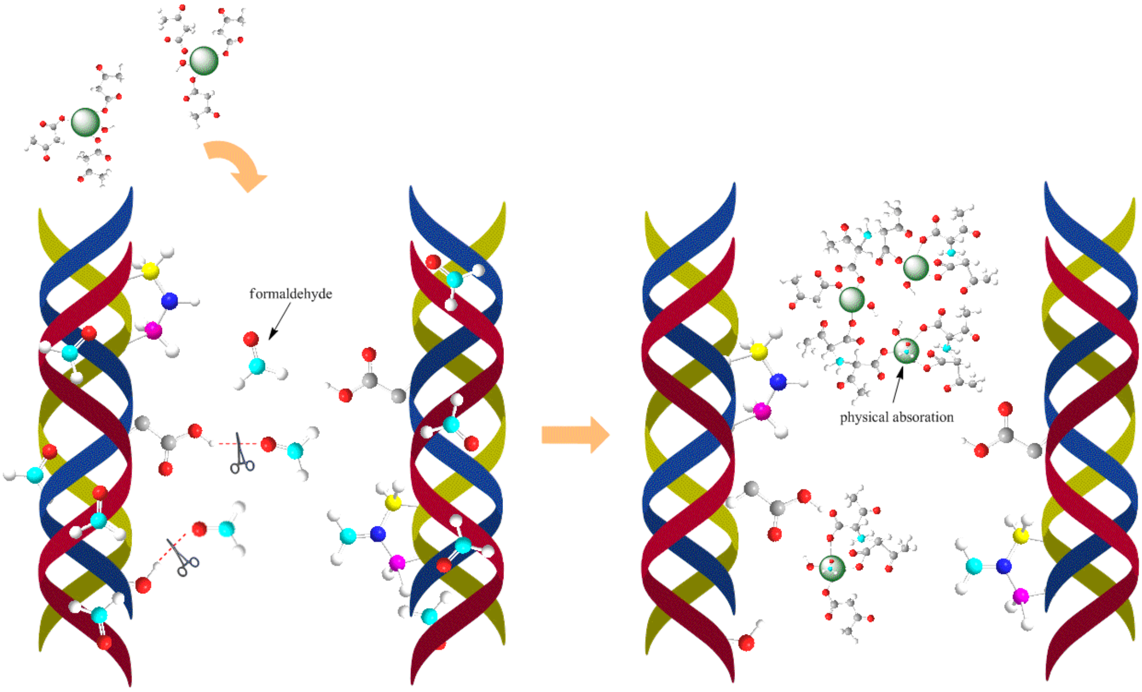


Fig.3 Particle size distribution of HAMP

3.2. The removal ability of formaldehyde in leather

HAMP was used in goatskin garment leather retanning to remove free formaldehyde. Three kinds of formaldehyde existed in collagen fiber which respectively are physical adsorption, hydrogen bond with hydroxyl and carboxyl groups in collagen fiber and covalent bonds between residuary formaldehyde with amino nitrogen in collagen fiber. HAMP is mainly used to remove the physically adsorptive and hydrogen bonding formaldehyde (Sheme 3).



Scheme 3 The mechanism between HAMP and formaldehyde in leather

The influence of reaction time and contents of HAMP on formaldehyde removal rate, were shown in Fig.4 and 5. As show in Fig.4 and Fig.5, higher dosage and longer time showed better removal performance. From Fig.4, we observed that the formaldehyde content in leather was reduced with the increase of HAMP content. When 4 wt% of wet blue leather was used, the formaldehyde content in leather were 167mg/kg which was less than the required standard 200mg/kg[24]. When the dosage of HAMP was 4 wt%, under different reaction time, the formaldehyde removal rate was shown in Fig.5. We could see that the removal rate reached the maximum when the time was 2.5h, after that the removal capacity of formaldehyde remain unchanged. The results revealed when 4 wt% of HAMP and 2.5h, the removal efficiency of formaldehyde achieved 88.4%.

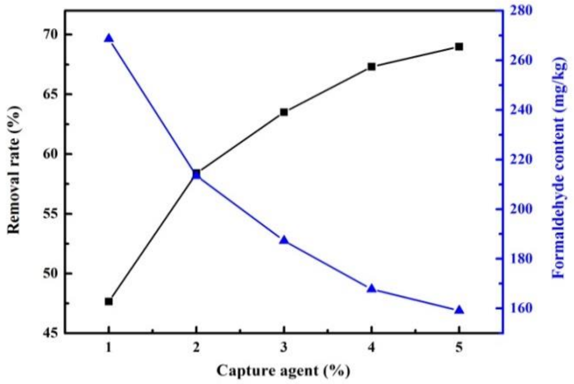


Fig.4. Effect of HAMP dosage on removal rate of HCHO

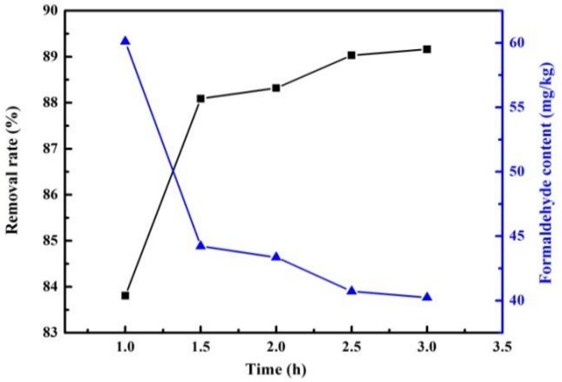


Fig.5 Effect of reaction time on removal rate of HCHO

Tab.3 Physical properties of leather

Samples	blank sample without HAMP	Sample treated with HAMP
Tensile strength (N/mm^2)	8.31	8.17
Tearing strength (N/mm)	29.54	22.57
Softness (mm)	7.9	8.5

The physical properties of leather were shown in Tab.3. As shown in Tab.3, the tensile strength and tearing strength reduced when HAMP was used. Meanwhile, the leather softness was improved. The reason may be that HAMP enter into fibers interior and plays the filling effect, which has a role of fiber dispersion. On the other hand, as dicyandiamide resin retanning agent, DESOATEN A-17 was synthesized by dicyandiamide and formaldehyde [25]. The reaction of HAMP and formaldehyde not only destroy the covalent bonds existing between residuary formaldehyde and collagen fiber, also inhibit the production of formaldehyde condensation hydroxymethyl dicyandiamide. The tearing strength of leather was slightly lower than that of leather without treated with HAMP, but it could satisfy the application effect of leather. Furthermore, in order to confirm the result, the leather was investigated by scanning electron microscope (SEM) and the results were shown in Fig.6. We observed that the collagen fibers of leather treated with HAMP with were loose, which further indicated that the increase of fiber spacing could strengthen leather softness.

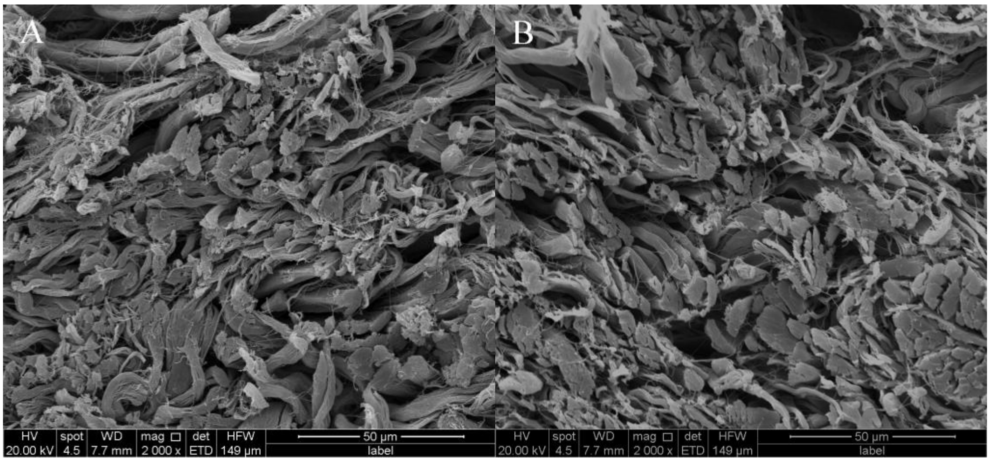


Fig.6 SEM of leathers before (A)and after (B)being treated with HAMP

4. CONCLUSIONS

In summary, a novel formaldehyde scavenger containing active methylene was synthesized by transesterification reaction of HBP and EAA. For its special structure, the removal form of formaldehyde including physical adsorption and chemical reaction. The results showed that the optimum HAMP dosage and reaction time were 4 wt% and 2h. The removal rate achieved to 88.4% and the formaldehyde content in leather was lower than limit standard. Meanwhile, collagen fibers became looser and the softness was improved, but the tensile strength and tearing strength of leather reduced.

ACKNOWLEDGMENTS

This work was supported by the Projects in the National Natural Science Foundation of China (NSFC, 21476134) and the innovation foundation of graduate student in Shaanxi University of science and technology.

REFERENCES

1 Dan Chen, Zhenping Qu, Yahui Sun, Yi Wang. Adsorption–desorption behavior of gaseous formaldehyde on different porous Al_2O_3 materials. Colloids and Surfaces A: Physicochemical and Engineering Aspects. **441**, 443–440, 2014,

2 Jean-Pierre Bellat, Igor Bezverkhyy, Guy Weber. Capture of formaldehyde by adsorption on nanoporous materials. Journal of Hazardous Materials. **300**, 711–717, 2015,

3 Michal Rivlin, Uzi Eliav, and Gil Navon. NMR Studies of the Equilibria and Reaction Rates in Aqueous Solutions of Formaldehyde. Journal of Physical Chemistry B. **119**, 4479–87, 2015,

4 Tunga Salthammer, Sibel Mentese, Rainer Marutzky. Formaldehyde in the Indoor Environment. Chemical Reviews, **110**, 2536–72, 2010,

5 Cheryl Hogue. Formaldehyde Deemed A Human Carcinogen.Chem. Eng. News Archive, **2**, 5, 2014,

6 Weihui Liang, Shen Yang, Xudong Yang. Long-Term Formaldehyde Emissions from Medium-Density Fiberboard in a Full-Scale Experimental Room: Emission Characteristics and the Effects of Temperature and Humidity.Environmental Science & Technology, **49**, 10349-10356, 2015,

7 Kun Lu, Wenjie Ye, Li Zhou et al. Structural Characterization of Formaldehyde-Induced Cross-Links Between Amino Acids and Deoxynucleosides and Their Oligomers. Journal of the American Chemical Society, **132**, 3388-3399, 2010,

8 Huang, Y., Han, M. F. The influence of α-Al_2O_3 addition on microstructure, mechanical, and formaldehyde adsorption properties of fly ash-based geopolymer products. Journal of Hazardous Materials. 193, 90−94, 2011,

9 Pei, J. J., Zhang, J. S. S. On the performance and mechanisms of formaldehyde removal by chemi-sorbents. Chem. Eng. J. **167**, 59−66, 2011,

10 Xu, Z. J.; Qin, N.; Wang, J. G.; Tong, H. Formaldehyde biofiltration as affected by spider plant. Bioresource Technollgy, **101**, 6930−6934, 2010,

11 N. Lu, J. Pei, Y. Zhao, R. Qi, J. Liu, Performance of a biological degradation method for indoor formaldehyde removal, Building & Environment. **57**, 253–258, 2012,

12 Y. Liao, C. Xie, Y. Liu, Q. Huang, Enhancement of photocatalytic property of ZnO for gaseous formaldehyde degradation by modifying morphology and crystal defect. J. Alloy. Compd. **550**, 190–197, 2013,

13 Liang, W. J.; Li, J.; Li, J. X.; Zhu, T.; Jin, Y. Q. Formaldehyde removal from gas streams by means of NaNO2 dielectric barrier discharge plasma. Journal of Hazardous Materials. 1**75**, 1090−1095, 2010,

14 K. Saulich, S. Mueller. Removal of formaldehyde by adsorption and plasma treatment of mineral adsorbent. Journal of Physics D Applied Physics. **46**, 844-851, 2012,

15 W Guo, Z Luo, H Lv, CL Hill. Aerobic Oxidation of Formaldehyde Catalyzed by Polyvanadotungstates. Acs Catalysis, **4**, 1154-1161, 2014,

16 T Cremer, SC Jensen, CM Friend. Enhanced Photo-Oxidation of Formaldehyde on Highly Reduced o-TiO2(110). Journal of Physical Chemistry C, **118**, 29242-29251, 2014,

17 P Hu, Z Amghouz, Z Huang. Surface-Confined Atomic Silver Centers Catalyzing Formaldehyde Oxidation. Environmental Science & Technology, **49**, 2384-2390, 2015,

18 Jiaguo Yu, Xinyang Li, Zhihua Xu, Wei Xiao. NaOH-Modified Ceramic Honeycomb with Enhanced Formaldehyde Adsorption and Removal Performance. Environmental Science & Technology, **47**, 9928–33, 2013,

19 J. Shah, M.R. Jan, S. Shah, M. Naeem. Spectrofluorimetric protocol for ceftriaxone in commercial formulation and human plasma after condensation with formaldehyde and ethyl acetoacetate, J. Fluoresc. **21**, 2155–2163, 2011

20 Song Niu, Hongxia Yan. Novel silicone-based polymer containing active methylene designed for the removal of indoor formaldehyde, Journal of Hazardous Materials. **287**, 259-267, 2015

21 GB 2912.2-2009 Textiles-Determination of formaldehyde (vapour absorption method).

22 Xu Zhengan. The synthesis of hyperbranched dispersant. Wuxi: Jiangnan University, 2008.

23 LIU Yan, SHEN Yi-ding, FEI Gui-qiang. Synthesis and Mechanism of Modified Poly(vinyl-alcohol) PAE Wet Strength Agent and Its Paper Strengthening Properties. Fine Chemicals, **32**, 1051-1055, 2015

24 GB 20400-2006 Leather and fur-limit of harmful matter.

25 Xie Heng, Shi Bi. Advances and Prospects of Amino Resin Retanning Agent. China Leather, **42**, 43-46, 2013

ECT O-31

ANALYSIS OF FLOW AND ENERGY ASPECTS OF ZERO LIQUID DISCHARGE (ZLD) TECHNOLOGY IN TREATMENT OF TANNERY EFFLUENTS IN TAMIL NADU, INDIA

Jakov Buljan*, K.V. Emmanuel, M. Viswanathan, M. Bosnić, I. Král'

In the course of conventional treatment of tannery effluent the composition of Total Dissolved Solids (TDS) somewhat changes but its total level remains virtually constant and considerably exceeds typical discharge norms. The global trend of processing of fresh hides, i.e. salt-free raw material is continuously expanding; for a host of reasons this approach is non-existent in India.

The precarious situation with water and soil pollution in the area of tannery clusters along the Palar River prompted the state environmental authorities to press for adherence to TDS discharge limits as well as to impose an approach not practiced in the tanning industry: a Zero Liquid Discharge (ZLD) concept.

Essentially, the ZLD systems concentrate dissolved solids by Reverse Osmosis (RO) and some kind of Multi Effect Evaporation (MEE) until only damp solid waste remains. Solid waste is disposed and nearly all water is reclaimed and reused. Accordingly, some of the existing Common Effluent Treatment Plants (CETPs) have been supplemented by RO and MEE, together with auxiliary steps (tertiary treatment, water softening etc.).

The analysis investigates and relates raw and equalized effluent inflows, RO feed, permeate and reject, evaporator feed and condensate and the yield of recovered, reusable water. Since the energy costs are critical for the viability of the entire concept, data about energy consumption (thermal, electrical main and Diesel) at key stages (RO, multistage evaporation) are consolidated, analysed and correlated. Additional energy needs and costs are compared with those for conventional (CETP) treatment and estimates made of the carbon footprint increase caused by the ZLD operations.

Keywords: TDS, ZLD, effluent flows, evaporation heat, energy consumption, energy costs, carbon footprint

INTRODUCTION

In the tanning area of Ranipet, Vellore District there are about 200 tanneries grouped in three clusters, each serviced by a CETP with treated effluent ultimately ending in the Palar River which in the recent years is mostly dry with no flow. There are neither sewerage networks nor sewage treatment plants in the adjacent municipalities.

Total Dissolved Solids (TDS), mainly chlorides and sulphates in tannery effluent have become the major environmental concern in arid and semi-arid regions as they make the receiving water recipients unfit both for livestock watering and for irrigation. Although a certain percentage emanates from pickling, deliming, tanning and wet finishing, the main source of TDS, especially of sodium chloride, is salt from preservation. It is estimated that worldwide at least 3.0 million tons of common salt per year are discharged into water recipients. Whilst specific discharge limits for TDS vary, generally they cannot not be achieved by conventional treatment.

Environmental damage caused by salting gradually prevails over its convenience aspects; the tanning industry in Europe has already largely switched to processing of salt-free raw material and this trend is continuously expanding (e.g. Brazil). For a host of reasons, while enforcing the TDS limit of 2100 mg/l, state environmental authorities and the tanning industry have chosen a different strategy: to adopt a Zero Liquid Discharge (ZLD) approach. The existing CETPs, following the usual treatment technology, have been supplemented by advanced, energy intensive methods like Reverse Osmosis (RO) and Multi Effect Evaporation (MEE) together with the necessary auxiliary steps (tertiary treatment, water softening etc.).

This paper attempts to analyse effluent flows, energy aspects and the impact on carbon footprint of the ZLD segment at three CETP+ZLD system(s) in Vellore District after a few years of operations. In that context, experience from the CLRI - UNIDO project in 1998-2000 in operating a pilot two-stages RO plant of 1 m^3/h capacity (albeit using solar pans instead of advanced evaporators) proved quite useful. The conclusion was that the system per se was technically viable but that O&M cost (only partly off-set by the price paid for fresh water) were quite prohibitive mainly due to high energy inputs.

Selection of plants for analysis

The plants selected cover the three main types of clusters: processing raw hides/skins to finished leather, (RANITEC), predominantly from raw to wet blue (VISHTEC) and from wet blue/EI to finished leather (SIDCO). The three plants basically follow the same technology, are operated by quite professional staff and the managements willing to cooperate. They are all connected to the Care AIR centre (server) of the TNPCB, the flow data are recorded in real time and counterchecks are possible.

Water consumption, effluent flows, yield

One claim is that addition of the ZLD stage has resulted in water consumption decrease from about 28 to only 11-12 l/kg of wet salted weight; increase in concentrations of pollutants support that claim. The opposing view is that local tanners already have long experience in economizing with water brought by tanks from considerable distances. To further halve such low consumption within 3 – 5 years is does not look quite likely. In addition, according to some UNIDO studies, the theoretical minimum is about 12 l/kg and it requires sophisticated recycling equipment.

The permeate from RO system and the condensate from evaporator are combined and distributed back to the tanneries through a recovered water conveyance system.

Table 2. Effluent flows, RANITEC, April 2015 – March 2016

ITEM	Unit	TOTAL	Average per month
Inflow to CETP	m^3	415,185	34,599
RO Feed	m^3	411,652	34,304
RO Feed vs. inflow	%	99 %	99 %
RO Permeate	m^3	296,331	24,694
Permeate vs. RO feed	%	72 %	72 %
RO Reject	m^3	115,321	9,610
RO reject vs. RO feed	%	28 %	28 %
Evaporator feed	m^3	118,632	9,886
Evaporator condensate	m^3	121,770	10,148
Evaporator condensate vs. evaporator feed, %	%	103 %	103 %
Total recovered Water	m^3	414,963	34,842
Total recovered water vs. RO feed %	%		102 %
Total recovered water vs. inflow to CETP %	%		101 %
Salt residue	tons	5,043	420
Salt residue vs. raw effluent, kg/m^3	Kg/ m^3		12.1

The (full) table shows some expected but also some perplexing figures and proportions.

- RO feed vs. inflow to CETP ratio varies from 81 – 114, average 99 %
- Permeate vs. RO feed varies from 57 – 80, average 72 %
- RO reject vs. RO feed varies from 20 – 43, average 28 %
- Evaporator condensate vs. feed varies from 97 – 109, average 103 %
- Total recovered water vs. RO feed from 96 – 106, average 102 %
- Total recovered water vs. inflow to CETP varies from 80 – 113, average 101 %
- Salt produced is 5043 tonnes, from 9.7 – 14.3 average 12.1 kg/m^3

For an accurate flow balance, it would be necessary to take into account additions such as water used for dissolving of chemicals and water from boilers as well as all losses (evaporation, sludge).

The main flow parameters for SIDCO and VISHTEC follow a similar pattern and are merged into a summary table.

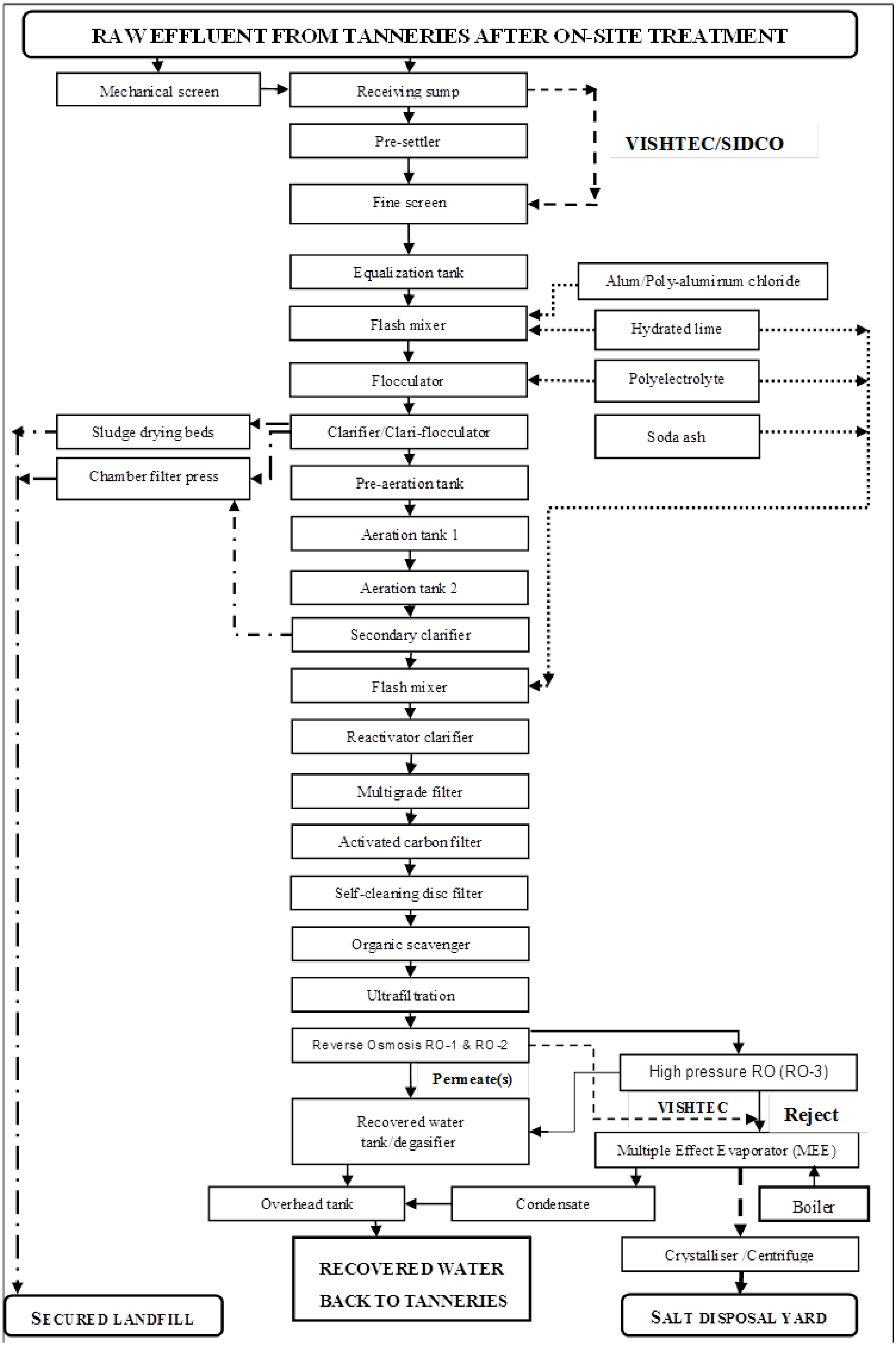
Table 3. Comparison of flow rates in three ZLD plants in tannery clusters in Vellore District

ZLD	RANITEC	SIDCO	VISHTEC
ITEM	Apr 15 – Mar 16	Sep 15 – May 16	Apr 15 – Mar 16
	Average flow rates and spans		
RO feed vs. inflow to CETP	99 % (81 – 114)	99 % (97 – 101)	101 % (99 – 104)
Permeate vs. RO feed	72 % (57 – 80)	76 % (67 – 83)	75 % (71 – 81)
RO reject vs. RO feed	28 % (20 – 43)	24 % (17 – 33)	25 % (19 – 29)
Total recovered water vs. inflow	101 % (80 – 113)	98 % (94 – 101)	101 % (97 – 105)
Total recovered water vs. RO feed	102 % (96 – 106)	97 % (94 – 101)	100 % (98 – 101)
Salt residue vs. raw effluent, kg/m^3	12.1 kg/m^3 (10.6 – 14.3)	6.2 kg/m^3 (4.7 – 8.5)	12.8 kg/m^3 (11.0 – 13.9)

Note: In the case of SIDCO, the inflow to CETP is actually the flow measured at the outlet of the equalization tank.

The overall flow balance is from the tanner’s viewpoint satisfactory: all losses due to evaporation (rather low due to high air humidity) and water removed with sludge are compensated by additions for dissolution of chemicals, water softening and washes. Ultimately, the effluent inflow coincides with the volume of water sent back to tanneries for reuse, its quality is superior to fresh water is due to low hardness.

Figure 10. A simplified flow-chart of the ZLD treatment at RANITEC, Vellore District



The ZLD is not so much treatment but rather a salt removal and sequestration system. For good results, it should operate with constant chemistry and constant flow for which they were specifically designed and must be monitored continuously. Preparatory, post-CETP "conditioning" steps, in particular water softening, often require dosing of different chemicals, including salts, which is quite a paradox for what is essentially a salt removal system.

The permeate from the RO system and the condensate from evaporator are combined and as the recovered water and metered distributed back to one-day storage capacity tanks in individual tanneries. The salt-laden solid residue is stored in bags in a huge salt storage yard.

Norms, monitoring

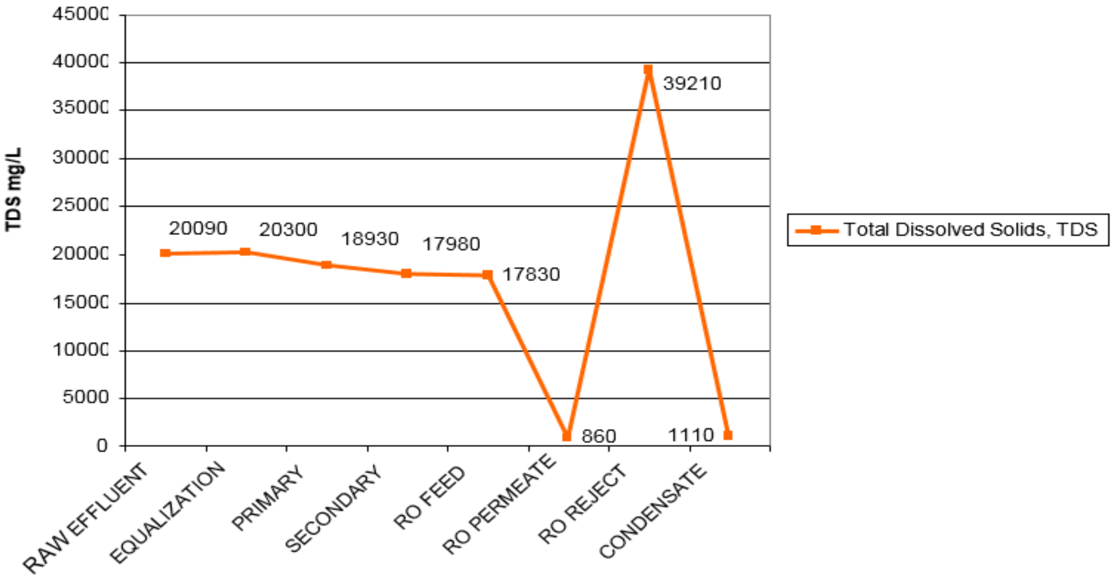
Water used in tanneries in clusters in the Vellore District is in most cases a mixture of water from own drilled wells and (better) water drawn from the Palar River bed further upstream and brought by tankers; the supply and characteristics of fresh water are inconsistent and unpredictable and comprehensive analyses of fresh water apparently are not available. Reportedly, the TDS of fresh water is in the range of 800-1500 mg/l, hardness 200-800 mg/l (tankers) and 1000 - 3000 mg/l, hardness 800-2000 mg/l (own wells). Thus, the usual problem of TDS is compounded by the high TDS/hardness level of fresh water.

To meet the TNPCB discharge norms for Dissolved solids (inorganic), 2100 mg/L, Chloride 1000 mg/L and Sulphates 1000 mg/L, a very different set up in the whole supply chain, mixing of treated effluent with municipal wastewater and/or advanced methods of decreasing the TDS level are required.

Unfortunately, differences in values found by CETP's own laboratories and analyses carried out by independent laboratories (third parties) too often exceed normal and acceptable variations. Inevitably, this casts a kind of shadow of doubt and possibly undue reserve in considering the laboratory statistical data.

The Computerized Operations Management System for the Ranipet CETP includes analytical data for key treatment units as well as sludge disposal record and sludge & leachate analysis.

Figure 11. Total Dissolved Solids (TDS), monthly averages, RANIPET, April 2015 – March 2016



Energy considerations

Energy consumption in tanneries depends on factors such as tannery location (geographic zone), production method, equipment, performance of electric motors, the ratio of manual vs. mechanical/automated handling (e.g. in moving the hides), drying methods, solid waste treatment, effluent treatment technology etc.

Generally, water (float) heating and drying, almost equally, make about two thirds of the energy consumption for leather processing itself. The type of energy source is also very relevant: fossil fuel (natural gas, coal, Diesel), renewable (wood, biomass) or self-generated renewable (solar energy, wind). Optimisation of electric motors, use of electric motors with higher efficiency and reducing the level of reactive energy are an important part of (electric) energy savings measures. The use Diesel generators is limited to emergencies.

Table 4. Energy consumption & cost, Primary, Secondary & Tertiary Treatment (PST), RANITEC, April 2015- March 2016

ITEM	Unit	TOTAL	Average per month
Inflow to CETP	m^3	415,185	34,599
Units consumed in KWh (EB)	kWh	2,349,980	195,832
Diesel litres (DG)	L	47,711	3,976
Units consumed in KWh (DG)	kWh	110074	9,173
Units consumed in KWh (EB+DG)	kWh	2,460,054	205,005
Total units vs. inflow	kWh/m^3		5.9
EB cost per unit	Rs.		9.1
EB power cost	Rs.	21,567,943	22,140,486
Diesel price	Rs./L	62	62
Cost of Diesel	Rs.	2,958,082	246,507
Total energy cost	Rs	24,526,025	2,043,835
Total energy cost vs. inflow	**Rs. /m^3**	**59 (USD 0.9)***	**59 (USD 0.9)***

*At Rs. 66.3 to 1 USD

Table 5. Energy consumption & cost, Reverse Osmosis + Evaporation, RANITEC, April 015- March 2016

ITEM	Unit	TOTAL	Average per month
Inflow to CETP	m^3	415,185	34,599
RO reject	m^3	115,321	9,610
Units consumed in kWh (EB)	kWh	4,168,830	347,403
Diesel litres (DG)	L	74,029	6,169
Units consumed in kWh (DG)	kWh	196,992	16,416
Units consumed in kWh (EB+DG)	kWh	4,365,822	363,819
Total units vs. inflow	kWh/m^3	10.0	10.0
EB cost per unit	Rs.	9.10	9.10
Total EB power cost	Rs.	37,492,478	3,124,373
Diesel price	Rs./L	62	62
Cost of Diesel	Rs.	4,589,798	382,483
Total power cost (EB + Diesel)	Rs.	42,082,276	3,506,856
Power cost (EB + Diesel)	Rs./m^3	101	101
Firewood used	Kg	7,406,396	617,200
Firewood price	Rs./kg	4.2	4.2
Firewood/m3 of reject	Kg/m^3	64	64
Cost of fuel (firewood) for MEE	Rs.	31,106,863	2,592,239
Total energy cost	Rs.	73,189,139	60,99,095
Total energy cost vs. inflow	**Rs./m^3**	**176 (USD 2.7)**	**176 (USD 2.7)**

The main energy parameters for SIDCO and VISHTEC generally follow a similar pattern and are merged into a summary table.

Table 6. Energy consumption & cost, Reverse Osmosis + Evaporation, RANITEC, SIDCO & VISHTEC 2015-2016

ITEM	**Average per month**			
	Unit	**RANITEC**	**SIDCO**	**VISHTEC**
Inflow to CETP	m^3	34,599	28,533	11,871
Units consumed in kWh (EB)	kWh	347,403	227,004	9,5795
Units per inflow	kWh	10.0	8.0	8.1
Total electricity cost (EB)	Rs.	21,567,943	1,407,422	593,928
Diesel consumed	L	6,169	1.193	732
Diesel cost	Rs.	382,483	73,959	45,353
Cost of power (EB + Diesel)/m^3	Rs./m^3	101	52	54
Firewood used	Kg	617,200	512,902	259,916
Firewood/m^3 of reject	Kg/m^3	64	77	88
Cost of fuel for evaporator	Rs.	2,592,239	2,277,283	1,143,632
Total energy cost	Rs.	6,099,095	3,756,618	1,833,784
Total energy cost vs. inflow	**Rs./m^3**	**176 (USD 2.7)**	**132 (USD 2.0)**	**154 (USD 2.3)**

Remark: Despite some variations, the price of firewood has been taken as Rs. 4.2/kg. Similarly, despite variations in Diesel prices during the year, its cost was calculated at Rs. 62/L as the yearly average; also, there are significant differences among plants in using Diesel as a source of energy.

Table 7. Comparison of energy consumption & cost, PST vs. ZLD stage (Reverse Osmosis + Evaporation), RANITEC, April 2015- March 2016

Item	**Unit**	**PST**	**ZLD**	**Total**	**Total vs. PST %**
		1	2	3 (1+2)	4 (3/1)
Inflow	m^3/year	415,185			
Electrical energy (EB)	kWh/year	2,349,980	4,168,830	6,518,810	277%
Total electrical energy vs. inflow	kWh/m^3	5.7	10.0	15.7	277 %
Cost of electrical energy (EB)	Rs./kWh	9.10			
Cost of electrical energy (EB)	Rs./year	21,384,818	37,936,353	59,321,171	277%
Cost of electrical energy (EB) vs. inflow	Rs./m^3	52	91	143	275%
Total electrical energy (EB) consumed in MJ	MJ/year	84,59,928	15,007,788	23,467,716	277%
Consumption of Diesel fuel	L/year	47,711	74,029	12,1740	255%
Diesel price	Rs./L	62			

Item	Unit	PST	ZLD	Total	Total vs. PST %
Cost of Diesel	Rs./year	2,958,082	4,589,798	7,547,880	255%
Consumption of fuel, Diesel in MJ	MJ/year	1,860,729	2,887,131	4,747,860	255%
Consumption of firewood	kg/year		7,406,396	7,406,396	
Cost of firewood per kg	Rs./kg		4.2	4.2	
Total cost of firewood	Rs./year		31,106,863	31,106,863	
Total firewood consumption, MJ	MJ/year		122,205,534	122,205,534	
Overall energy consumption (EB+Diesel+ firewood)	MJ/year	10,320,657	140,100,453	150,421,110	1457%
Total energy cost (EB+Diesel+ firewood)	Rs./year	24,342,900	73,633,014	97,975,914	402%
Total energy in MJ vs. inflow	**MJ/m^3**	**25**	**337**	**362**	**1457%**
Total energy cost vs. inflow	**Rs./m^3**	**59**	**177**	**236 (USD 3.6)**	**402%**

Note: Minor discrepancies due to rounding up!

The following table shows shares of the main components of energy consumption and costs.

Table 8. Energy consumption & cost comparisons, RANITEC, April 2015- March 2016

Item	Rate %
Share of PST energy in Total energy consumed	7%
Share of ZLD energy in Total energy consumed	93%
Share of PST energy cost in Total energy cost	25%
Share of ZLD energy cost in Total energy cost	75%
Share of electrical energy in Total energy consumed, MJ	16%
Share of thermal (Diesel) energy in Total energy consumed. MJ	3%
Share of thermal (firewood) energy in Total energy consumed. MJ	81%

* including Diesel Values rounded up!

The impact of addition of the ZLD stage (RO + MEE) to the conventional treatment can be summarizedas follows:

- The consumption of electrical energy went up nearly three times
- The overall energy consumption (electrical and thermal) went up nearly 15 times
- The cost of electrical energy, including its unit cost (Rs./m^3) went up nearly three times
- The total cost of energy (electrical and thermal) went up about 4.5 times
- The share of ZLD energy in total energy consumed is about 94 %
- The share of ZLD energy cost in total energy cost is about 78 %

Chemicals from the ZLD stage, O&M costs, salt residue

In addition to the usual chemicals used during the primary treatment (lime, alum, polyelectrolytes) significant amounts of chemicals affecting the TDS content are added during tertiary treatment, water softening, RO and evaporation steps: hydrochloric acid, sodium metabisulphite, antiscalant, polyphosphates, caustic soda, sodium bicarbonate etc.

The reported, indicative O&M cost for the year 2015/2016 are between USD 6.9 – 8.7/m^3, part of it assumingly offset by saving the cost of fresh water of about USD 1.4/m^3. In absence of reliable data about raw material input, yields etc. it is not possible to relate the O & M cost to leather output, educated guesses put them from about Rs. 20/m^2 (RANITEC), Rs. 23/m^2 (SIDCO) to Rs. 40/m^2 (VISHTEC), corresponding to USD 0.30, USD 0.35 and USD 0.60 per square metre.

The salt residue represents a very serious environmental challenge, quantities generated are impressive. Only in year 2015/2016, the RANITEC plant has produced 5043 tonnes, VISHTEC 1818 tonnes and SIDCO 1591 tonnes. Unfortunately, currently there are substantial differences between the theoretical values for the RO + Evaporation stage and the actual outputs of salt residue at three plants considered.

Table 9. Apparent gaps in TDS balance at RO stage, tonnes per year

Item	Unit	RANITEC	VISHTEC	SIDCO*
RO feed	m^3/year	411,652	143,753	254,955
TDS in RO feed	mg/L	17,830	17,920	9,160
TDS in RO Feed	t/year	7,340	2,576	2,335
Permeate	m^3/year	296,331	108,315	194,113
TDS in permeate	mg/L	860	465	388
TDS in permeate	t/year	255	50	75
Reject	m^3/year	115,321	35,438	60,842
TDS in Reject	mg/L	39,210	39,420	36,100
TDS in Reject	t/year	4,522	1,397	2,196
TDS in permeate + TDS in Reject	t/year	4,777	1,447	2,271
Difference: TDS in RO Feed – (TDS in permeate + TDS in Reject)	t/year	**2,563**	**1,129**	**64**
Difference	%	**35 %**	**44 %**	**3 %**

*actually for nine months only

There are views and computations suggesting substantially lower figures. According to them, the unaccounted loss at RANITEC is 4.65 %, at SIDCO 3.72 % and only 0.15 % at VISHTEC. However, some logic and estimates in those computations such as the share of Volatile portion of salt lost in evaporation or in transportation and some other are very questionable. Obviously, the complexity of the issue requires extensive, independent monitoring and analysis over at least one year.

Carbon footprint - the impact of ZLD stage on CO_2 emissions

Values used for computations:

- Average CO_2 emissions for electricity production in India: 0.9.kg CO_2/kWh (2012)[1]
- Calorific value of Diesel used by DG: 39 MJ/L
- CO_2 emissions from Diesel: 74.1 kg CO_2/GJ of thermal energy[2]
- CO_2 emission/L of Diesel: (39 x 74,1)/1000 = 2.9 kg CO_2/L of Diesel
- Calorific value of firewood used by evaporation boilers: 16.5 MJ/kg
- CO_2 emissions from firewood burning: 109.6 kg CO_2/GJ of thermal energy[3]
- CO_2 emission/kg of firewood: (16.5 x 109.6)/1000 = 1.8 kg CO_2/kg of firewood
- COD of effluent before biological treatment: 2490 mg O_2/L
- COD of effluent after secondary clarifier: 260 mg O_2/L
- COD degraded during biological treatment: (2490 – 260)=2230 mg O_2/L
- Estimated COD : TOC ratio: 3 : 1
- CO_2 : TOC ratio: 3.67 : 1

Table 10. Leather production, flow, electrical energy & firewood consumption at the CETP+ ZLD plant RANITEC, 2015-2016:

Item	Unit	CETP	ZLD	Total CETP & ZLD
Total estimated leather produced	sq.ft	96,353,038		
Total estimated leather produced	m^2	8,951,486		
Flow	m^3/year	415,185		
Consumption of electrical energy (EB)	kWh/year	2,349,980	4,168,830	6,518,810
Consumption of Diesel	L/year	47,711	74,029	12,1740
Consumption of firewood	kg/year		7,406,396	7,406,396

Based on above values and data it is possible to derive figures for the CF pertaining to the RANITEC plant and relate them to the estimated leather output.

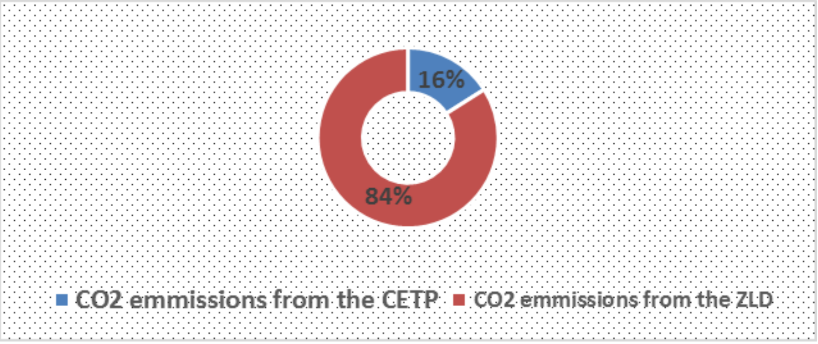
Table 11. CO_2 emissions from the CETP + ZLD plant RANITEC, March 2015 – April 2016

Item	Unit	CETP	ZLD	Total CETP & ZLD
Total estimated leather produced	sq.ft	96,353,038		
Total estimated leather produced	m^2	8,951,486		
Flow	m^3/year	415,859		
Consumption of electrical energy (EB)	kWh/year	2,349,980	4,168,830	6,518,810
Consumption of Diesel	L/year	47,711	74,029	121,740
Consumption of firewood	kg/year		7,406,396	7,406,396
COD removed	kg/year	927,366	-	-
TOC removed during biological treatment	kg/year	309,122	-	-
CO_2 emissions from consumption of electrical energy (EB)	kg/year	2,114,982	3,751,947	5,866,929
CO_2 emissions from Diesel	kg/y	138,362	214,684	353,046
CO_2 emissions from biological treatment	kg/year	1,134,478		1,134,478
CO_2 emissions from firewood for MEE boiler	kg/year	-	13,331,513	13,331,513
Total CO_{2e} emissions, year	**kg/y**	**3,387,822**	**17,298,144**	**20,685,966**
Total CO_{2e} emissions, year	**tonnes/year**	**3,388**	**17,298**	**20,686**
Total CO_{2e} emissions, %	**%**	**16**	**84**	**100**
CO_{2e} est. emission vs. leather production	**kg/sq.ft**	**0.04**	**0.18**	**0.22**

Note: The figures about CO_2 emissions include neither leather processing nor sludge disposal, they pertain only to conventional effluent treatment (CETP) and RO and evaporation stage (ZLD) albeit without disposal of residual salt.

In summary, the ZLD stage has increased the CO_{2e} emissions of the RANITEC plant by about six times.

Figure 12. Shares of CETP & ZLD stages in the total CO_2 emissions, RANITEC, 2015-16



CONCLUSIONS

The dramatic situation with water and soil pollution along the Palar River together with public and buyers' pressure eventually prompted the TNPCB to enforce the discharge limit for Dissolved solids (inorganic) of 2100 mg/L; apparently, the ZLD system was imposed as the only approach to supplement the conventional treatment.

Reportedly, this has resulted in water consumption close to the theoretical minimum (12 m^3/tonne) and substantial underutilization of CETP & ZLD plants. A very strong opposing view is that i) the tanners from the area already had a long experience in economizing with water ii) rather complex water saving and float recycling system is required to achieve such low level iii) the necessary technology modifications take time and that iv) a close, independent scrutiny is needed to verify this claim.

The average yearly flow rates along the treatment line in three ZLD plants considered are: the RO feed vs. inflow from 99 to 101 %, RO permeate vs. RO feed 72 – 76 %, RO reject vs. RO feed 24 – 28 % and the total recovered water vs. inflow 97 – 102 %.

The energy impact of the ZLD stage in relation to the conventional treatment are as follows:

- The consumption of electrical energy went up nearly three times
- The overall energy consumption (electrical and thermal) went up nearly 15 times
- The cost of electrical energy, including its unit cost (Rs./m^3) went up nearly three times
- The total cost of energy (electrical and thermal) went up about 4.5 times
- The share of ZLD (RO+MEE) energy in total energy consumed is about 94 %
- The share of ZLD (RO+MEE) energy cost in total energy cost is about 78 %

The reported, indicative O&M cost for the year 2015/2016 are between USD 6.9 – 8.7/m^3, part of it assumingly offset by saving the cost of fresh water of about USD 1.4/m^3.

The salt residue produced poses a very serious environmental challenge; in 2015/2016 it was 5043 t (RANITEC), 1816 t (VISHTEC) and 1591 t (SIDCO). Unfortunately, there are substantial differences between the theoretical values and the actual outputs; large quantities are “missing” without convincing explanation.

Computing average CO_2 emissions for electricity production in India, calorific value of firewood used by evaporation boilers, CO_2 emissions/kg of firewood, COD degraded during biological treatment, estimated COD/TOC ratio and CO_2/TOC ratio, it works out that the ZLD stage has increased the CO_{2e} emissions at RANITEC by more than six times.

There is no doubt that industrial scale ZLD in treatment of tannery effluents is technically feasible, advanced technologies applied impressive, recycling of the purified water is both logical and practical. However, the system is not robust and a viable solution for reutilization and/or safe disposal of solid residue is not in sight; moreover, within about three years O & M cost may exceed the installation cost.

It is quite late but possibly not too late to thoroughly (re)consider potential alternatives, a combination of short- and long-term options such as construction of proper sewage systems & WWTW in the townships in the Vellore District, simultaneous strong support to organized slaughter of some livestock (buffaloes, goats/sheep) and salt-free preservation, concentration of wet blueing works etc.

Finally, further work by a multidisciplinary ground team is needed to closer study issues such as detailed water mass balance, the exact impact of chemicals added and changes in the TDS composition along the process, optimization of auxiliary processes (ultrafiltration, water softening), possibly establish a more rigorous data recording etc.

ACKNOWLEDGMENTS

The authors appreciate the cooperative spirit and the willingness of the managements of the CETPs to provide the basic data used for preparing the analyses presented in this paper. Views and comments by C. Money are also gratefully acknowledged.

REFERENCES

Selected UNIDO documents

1. Bosnić M, Rajamani S, Sahasranaman A, Ultrafiltration application in tannery waste water treatment, 1998
2. Bosnić M, Multiple stage evaporation system to recover salt from tannery effluent, 1998
3. Buljan J, Bosnić M, Sahasranaman A, Comparative evaluation of environmental priorities and treatment costs in the tanning sector in industrialized and developing countries, Parallels: France – Italy – India, 2002
4. Buljan J, Costs of tannery waste treatment, 2005
5. Buljan J, Introduction to treatment of tannery effluents, 2011
6. Buljan J, Král I, Bosnić M, Daniels R, Pollutants in tannery effluents - Sources, description, environmental impact, 2013 (Revised edition)
7. Emmanuel KV et al, Operation of pilot Reverse Osmosis (RO) unit at ATH Leder Fabrik, Melvisharam, India, 2001
8. Sampathkumar S et al, Management of Total Dissolved Solids (TDS) in tannery effluent, 2000
9. Sampathkumar S, Viswanathan M, Desalting of raw hides/skins and reuse of dusted salt in pickling operation, 2002

Other sources

10. Buljan J, Some considerations about the problem of salinity of tannery effluents, LGR Tagung 2004
11. Emmanuel KV, ILIFO & Personal communications, 2016
12. Money C.A. (1999), Clean technology challenges, Science and technology for leather into the next millennium, Tata McGraw Hill Publishing Company, New Delhi, pp. 284-294.
13. Pfisterer H, Energieeinsatz in der Lederindustrie, Bibliothek des Leders, Band 9,1986
14. Subramanian S, et al. Green Solution for Salinity in Tannery Waste water: A Step Forward in Leather Processing, JALCA 109, July 2014
15. Ranipet Tannery Effluent Treatment Co. Ltd., RANITEC brochure 2105, www.RANITEC.com
16. Performance evaluation/adequacy assessment of Pertec CETP, Indian Leather Industry Foundation (ILIFO), August 2015
17. Performance evaluation/adequacy assessment of Amburtec Thuthipet CETP, Indian Leather Industry Foundation (ILIFO), August 2015
18. Poncet T, et al., Eco-Design: Life Cycle analyses show that energy is a key factor for the environmental impact of leather and might save money, IULTCS Congress, 2011
19. Rao JR at al. A Polymer-Based Preservation, www.aaqtic.org.ar/congresos/china2009
20. Ramos M A, Development of an alternative low salt hide preservation using dehydrating agent (PEG), sanitizer and crude glycerol, ALCA Convention 2014

21. JALCA, several issues of the ezine version
22. World Leather, several issues
23. Various open sources (Wikipedia, etc.), http://www.physchem.co.za/Heat/Latent.htm

START-UP OF SIMULTANEOUS REMOVAL OF NITROGEN AND ORGANIC CARBON FROM SYNTHETIC TANNERY WASTEWATER USING AIRLIFT SEQUENCING BATCH REACTOR

Aysanew Gorems Melesse*, S.V Srinivasan, P.C.Sabumon, Berhanu Assefa Demissie

Leather Industry Development Institute, P.O.Box 24692 code 1000, Addis Ababa Ethiopia
CSIR-Central Leather Research Institute, Adyar, Chennai, 600 020, India
VIT University,Environmental, Water Resources & Transportation Engineering Division ,School of Mechanical & Building Sciences (SMBS) Vandalur -Kelambakkam Road Chennai - 600 127, Chennai India.
School of Chemical and Bio Engineering, Addis Ababa Institute of Technology, Addis Ababa University, P.O. Box 385, Addis Ababa, Ethiopia

The present study employed airlift sequencing batch reactor system to develop the simultaneous removal of nitrogen and organic carbon from synthetic tannery wastewater by seeding with conventional tannery aerobic sludge. The reactor (working volume of 5L) was run for 61d at by automated control of the SBR cycles, pH, DO and temperature. The reactor was run at 18 at constant 50% volume exchange ratio. The performance of the reactor was evaluated interms of TCOD, sCOD, BOD, TKN, NH4-N, NO3-N, NO2-N, DO and pH profiles. At the start of the operation, the reactor was run at an HRT of 10d resulting in MLSS of (3.5-4g/L), during these periods, the reactor shows no conversion or removal of the ammonical nitrogen for the first 30d an indication that the nitrifier's population in the seed sludge was very less. Ammoncal nitrogen conversion started after 30 days of operation. During this time, the reactor shows almost complete carbon removal and unstable partial nitrification to nitrite with very less conversion to nitrate. Evaluation of the performance of the reactor at steady state shows a 94.6% COD, 80±5%NH4-N and 43%TN removal efficiency.

Key words: SBR, Cycle time, Nitrification, Denitrification

1. INTRODUCTION

Tannery wastewater is characterized by high organic carbon and nitrogenous compounds due to the raw material (raw hides/skins/ and chemicals) used in making leather. The major form of nitrogen in tannery wastewater are organic N originated from the breakdown of nitrogenous compounds from processed hides and skin and ammonical nitrogen (NH_4-N) originated from deliming operation(Bosnic, Buljan et al. 2000; Leta, Assefa et al. 2004).The common nitrogen compounds present in a wastewater treatment plant which may adversely impact the receiving water are Ammonium ions (NH_4^+), Nitrite ions (NO_2^-) and Nitrate ions (NO_3^-).The discharge of too high nitrogen concentrations into the receiving waters without proper treatment caused dissolved Oxygen (O_2) depletion, Toxicity, Eutrophicaiton i.e.excessive growth of algae, Methamoglobinemia i.e blue baby syndrome and deterioration of Water aesthetic quality and odours from decomposing algae(Gerardi 2003).

Biological removal of nitrogen is comparatively the most economical option for industrial and municipal wastewaters(Münch, Lant et al. 1996; Henze 2008). Conventionally, it is carried out by a process called nitrification and denitrification. Nitrification is a two step biological process where ammoinical nitrogen is first converted to nitrite by ammonium oxidizing bacteria (AOB) and further oxidized to nitrate by nitrite oxidizing bacteria (NOB). These groups of bacteria are chemolitoauthotrophs and consume bicarbonate as source of carbon. Biological denitrification is a reduction of nitrate to nitrogen gas by hetrotrophic bacteria in the presence of organic carbon as terminal electron acceptor under anoxic condition. Nitrification is the rate limiting step in biological nitrogen removal and the wastewater C/N ratio is very important for effective nitrogen removal. For wastewater having low C/N ratio an external carbon source is usually provided(Henze 2008). Recently some researchers prefer the short-cut partial nitrification denitrification where the ammonia is first converted to nitrite and then denitrified in the presence of organic carbon. This process help significant saving in energy and cost of operations(Sinha and Annachhatre 2007).In the absence of organic carbon and the presence of ammonical nitrogen and nitrite, removal of nitrogen is also possible under anaerobic condition by Anammox bacteria(Strous, Heijnen et al. 1998).

Primary Pysico-chemical treatment such as screening, flow equalization, coagulation, flocculation and sedimentation followed by extended aeration system is the most widely used treatment scheme used for tannery wastewater. Extended aeration system with higher HRT and SRT is employed for nitrification. Besides, external carbon source is usually added in the denitrification process to maintain the C/N ratio above 5. This conventional tannery wastewater system is less effective and costly since there is always large variation in tanning practices and wastewater(Abdallh and WalidSayedAbdelhalim 2016). Sequencing batch reactor (SBR) technology is advantageous than the extended aeration process due to their flexibility and higher COD and nitrogen removal rates at comparatively shorter HRT (Ganesh et al. 2006). The SBR technology provides a possibility of influencing the microbial system in the reactor(Dohare and Kesharwani 2014). Many modifications in SBR technology such as continuous flow SBR, sequencing batch biofilm reactor, combined anaerobic–aerobic SBR have been developed to have functions of biological carbon oxidation, nitrification and denitrification, and phosphorus removal. Studies on the application of SBR technology in laboratory, pilot and large-scale treatment systems for tannery wastewater have been reported by some authors (Farabegoli et al. 2004; Ganesh et al. 2006; Murat et al. 2006). Despite the large number of studies in simultaneous removal of organic carbon and nitrogen from various wastewater streams, no systematic approach to simulate tannery wastewater and study the removal dynamics in SBAR has been done sofar. The current work employed a specially designed SBAR system with central draft tube arrangement. The draft tube provides adequate mixing by airlift movement and at the same time supplying dissolved oxygen. It is also provided with online monitoring and control of pH DO, temperature and SBR cycle times. Daily monitoring of the reactor performance along with kinetics studies at some fundamental days of operation was used to evaluate and optimize the performance of the reactor.

2. MATERIALS AND METHODS

2.1. Composite tannery wastewater

Raw composite tannery wastewater was brought from the equalization tank of Ranitec CETP and characterized for basic parameters, Table 1.

2.2. Synthetic tannery wastewater

Synthetic tannery wastewater was prepared based on the characteristics data (Table 1) and the literatures(Faouzi, Merzouki et al. 2013; Anjali and Sabumon 2014).

Commercial milk powder (Nesttle Everyday) was used as sole source of COD and Organic N. One gram of milk powder was dissolved in luck warm water and analyzed for COD and TKN. The analysis was repeated several times and the result used for calculating the amount of milk powder required simulating the composition in composite tannery wastewater, Table 2.

2.3. Seed sludge

A 5L aerobic sludge from aeration tank of Ranitech CETP and 5L anoxic Sludge from anoxic tank of Vanitech CETP was brought to the lab and settled and washed with tap water and phosphate buffer and mixed in 3:1 volumetric ratio. A volume 1.5L of the mixed sludge was initially inoculated into the reactor.

2.4. Airlift Sequencing Batch reactor

A specially designed SBAR with central draft tube for mixing and aeration was used for the study. The cylindrical reactor was constructed with plexi glass and had a nominal dimension of 80cm height, 10.0cm diameter, and 64cm effective liquid depth and 5L liquid capacity. It has a 16cm headspace and 60.5cm long central draft tube with aeration perforations at the bottom of the tube. Air is supplied at the top of the reactor down to the tip of the draft tube and released at the bottom whereby creating mixing and aeration. The draft tube was designed in such a way that there were uniform mixing, aeration and ease of cleaning. This system reduces the need to have additional mixing arrangement during aeration. The reactor is equipped with influent peristalitic pump, air blower, acid and alkali feed pumps, pH, DO and Temperature sensors, solenoid valves and effluent collection tank. The operations of the reactor were controlled by PLC controller. The controller is linked with input measurements from pH sensor, DO sensor, temperature sensor and timer. The schematic diagram of the SBAR is depicted in Figure1

2.5. Operation of the reactor

The reactor was filled with 1.5L of seed sludge and make up to 5L of the reactor volume with synthetic wastewater of composition in table 2&3. Aeration was started and at the end of the aeration the reactor mixture was allowed to settle for 30min and 2.5L of the supernatant decanted at the end of the cycle. The reactor was run at 10d SRT resulting in MLSS (3.5-4g/L). The MLSS was measured every two days and calculated amount of the excess sludge was withdrawn from the reactor.

The reactor was operated at room temperature (29-31^{0}C). The pH was controlled online throughout the operating days, 0.25M $NaHCO_3$ and 0.25MHCL solutions were used to maintain the reactor pH in the range (7.25-7.3). A relatively alkaline pH was very important for selective enrichment of AOB and therby maintain partial nitrtification to nitrite(Kim and Seo 2006). The DO was controlled at 1mg/L through an on-off control of the air blower. Maintaining low DO elevated the growth yield of ammonia oxidizers by double but with a reduced substrate utilization rate (Hanaki et.al, 1990).

The cycle time was also controlled by setting sequentially the time for feeding, aeration, settling and decanting. The feeding time was 9min, settling 30min and decanting 6min. The reactor is operated at 50% volume exchange ratio and at the end of every cycle 2.5L of reactor volume is drained.

2.7. Kinetics Study

At some fundamental operating dates when the reactor shows steady state performance, kinetics study was conducted for TCOD, sCOD, BOD,TKN, NO3-N, NO2-N, Alkalinity, pH, DO, and MLSS/MLVSS for complete cycle time.

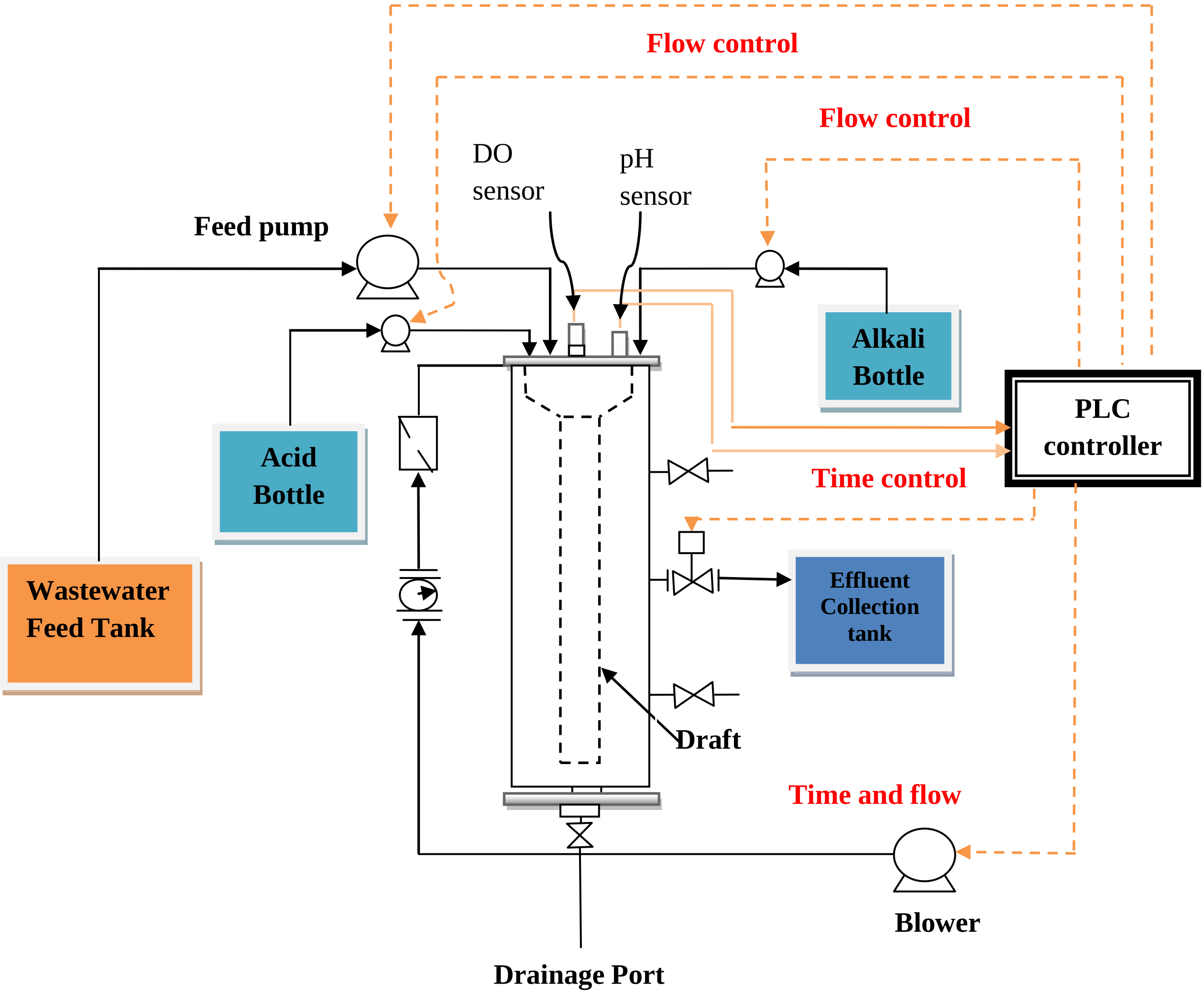


Figure 1: Schematic diagram of the SBAR system

Table 1: Characteristics of combined tannery wastewater (analytical values represent the average of 10 analysis)

S/N	Parameters	Values[a]
1	pH	7-9
2	suspended solids (mg/L)	2500-3500
3	COD (mg/L)	3500-6500
4	BOD_5, 20 °C	1400-3000
5	Sulphate (mg/L)	1500-3000
6	Sulphide (mg/L)	20-40
7	TKN (mg/L)	400-550
8	NH4-N (mg/L)	100-400
9	Chromium (III) mg/L	50-70
10	Chloride (mg/L)	5000-8500
11	TDS (mg/L)	12,000-20,000

[a] Each parameter was analyzed 10 times

Table 2: Composition of synthetic tannery wastewater used for the study

S/N	Name of chemical	Amount (mg/L)	Equivalent values
1	Milk powder (industrial grade Nesttle Everyday milk powder)	2500	TCOD 4500-6000mg/L[a] sCOD equivalent 3000-3600mg/L[b] Org-N equivalent 150-160mg/L[c]
2	(NH4)2SO4	1378	NH4-N equivalent 250-290mg/L[d] TKN equivalent 400-450mg/L[e]
3	MgSO4.7H2O	25	
4	FeSO4.7H2O	20	
5	KH2PO4	88	
6	K2HPO4	90	
7	Na2CO3	66	
8	NaHCO3	105	
9	CaCl2.2H2	30	
10	Trace Element solution	1ml	

[a,b,c,d, e] are measured values for 10 analysis

Table 3: Chemical composition of trace element solution

S/N	Name of chemical	Amount(mg/L)
1	$FeCl_3.H_20$	1500
2	H_3BO_3	150
3	KI	30
4	$MnCl_2.4H_2O$	120
5	NaMnO4.H2O	60
6	$ZnSO_4.7H_2O$	120
7	$CaCl_2.2H_2O$	150
8	CuSO4.5H2O	30

Result and Discussion

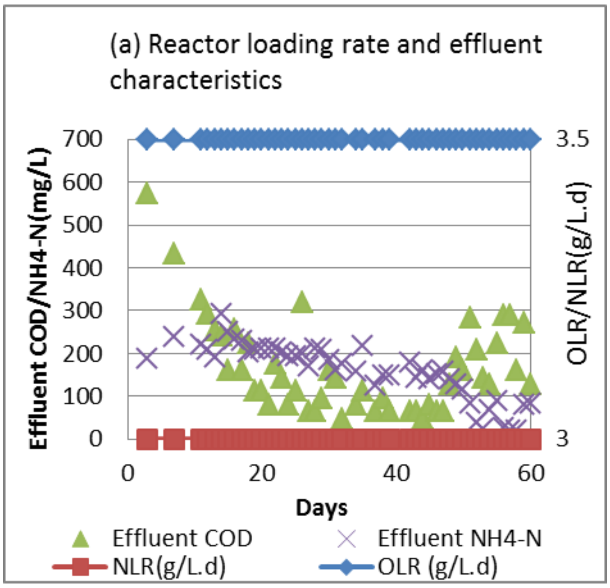
The results of the start up of the reactor are described in figure 2. The results are presented interms of the reactor loading rate applied (Figure 2(a), the removal efficiency interms of COD (Figure 2(b) , NH4-N (Figure 2 (c) and total nitrogen (Figue 2(c). Besides removal kinetics in one complete cycle interms of COD, NH4-N, NO3-N, NO2 (Figue2 e, f, g,h) are also discussed.

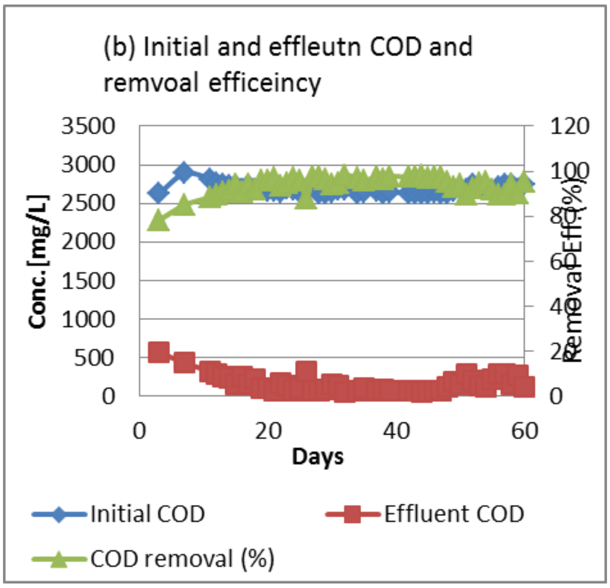
The first 60 days of the reactor operation shows the start up time, nitrite accumulation and denitrification via nitrite. The start-up and operation of the SBAR during this phase involved the control of pH, DO, HRT, SRT and temperature, which favour a conducive environment for HB and AOB and non-conducive environment for NOB's

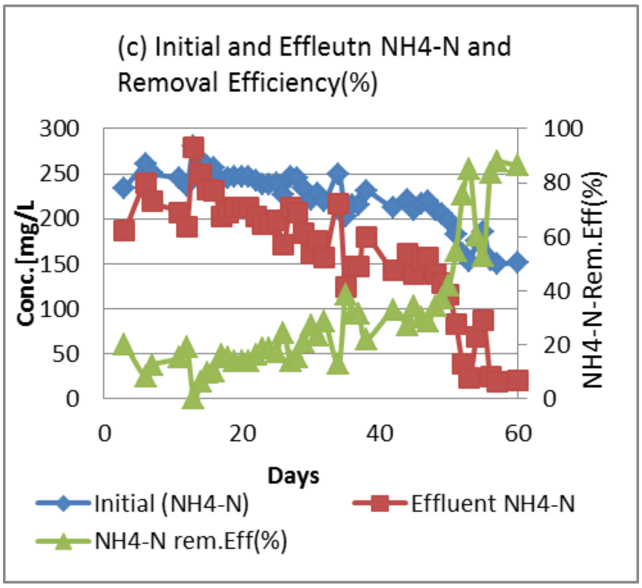
The reactor loading rates interms of organic lading was 3.5g/L.d and interms of nitrogen was 0.236g/L.d and the COD removal starts in just two days of the reactor operation while the ammonia removal started after 30 days of operation. Figure 2 (b) shows the initial mixed liquor and effluent COD concentration s and the associated removal efficiency, as the graphs shows the efficiency was above 90% during whole start up period. Figure 2(c) shows the initial mixed liquor and effluent NH4-N concentrations and associated removal efficiency. The graphs shows improved NH4-N removal the start up period (days 30) . Figure 2(d) shows the total nitrogen removal efficiency and the graphs shows higher removal efficiency after the start up of nitrification (day 30) indicating that nitrification is a rate limiting step in total nitrogen removal.

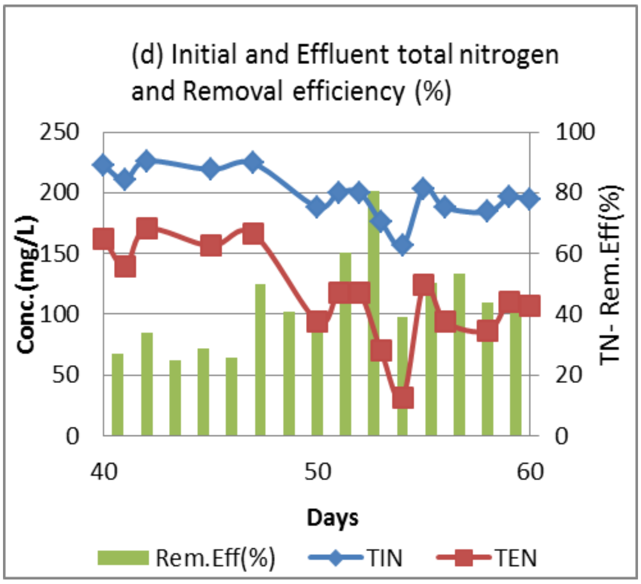
Figure 2((e), (f), shows the NO2-N and NO3-N, NH4-N and COD profile at steady state operation. This profile clearly shows the ammonia conversion in one complete cycle time (18hrs). All the profiles show increasing NO2-N and NO3-N concentrations but the increase in NO2-N is very high and for NO3-N was insignificant. While Figure 2((g) and (h)) shows the profile including NH4-N and COD respectively. This profiles shows decrease in both COD and NH4-N and increase in NO2-N and NO3-N as a result of the ammonia oxidation. The graphs clearly show partial nitrification of NH4-N to NO2-N.

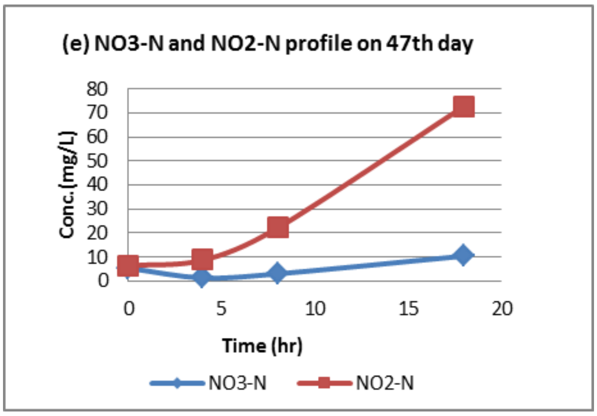
There was insignificant oxidation of nitrite to nitrate during this phase of operation, this indicates relatively higher start up period required for NOB compared to AOB and hetrotrophs (Ganesh, Sousbie et al. 2015) and the relatively higher pH and low SRT maintained favor AOB more than NOB. The SRT was maintained in the range 10days resulting in MLSS of (3500-4000mg/L). Partial nitrification and organic carbon removal was achieved, denitrification plays a role in the organic carbon removal mainly during the anoxic feeding and initial period of aeration. During this phase of operation, the reactor shows 94.6%COD removal, 80% NH4-N oxidation to nitrite and 43%TN removal under steady state.

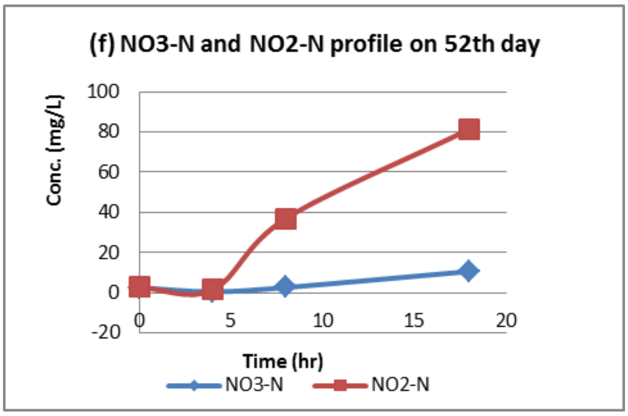

(a) Reactor loading rate and effluent characteristics


(b) Initial and effleutn COD and remvoal efficeincy


(c) Initial and Effleutn NH4-N and Removal Efficiency(%)


(d) Initial and Effluent total nitrogen and Removal efficiency (%)


(e) NO3-N and NO2-N profile on 47th day


(f) NO3-N and NO2-N profile on 52th day

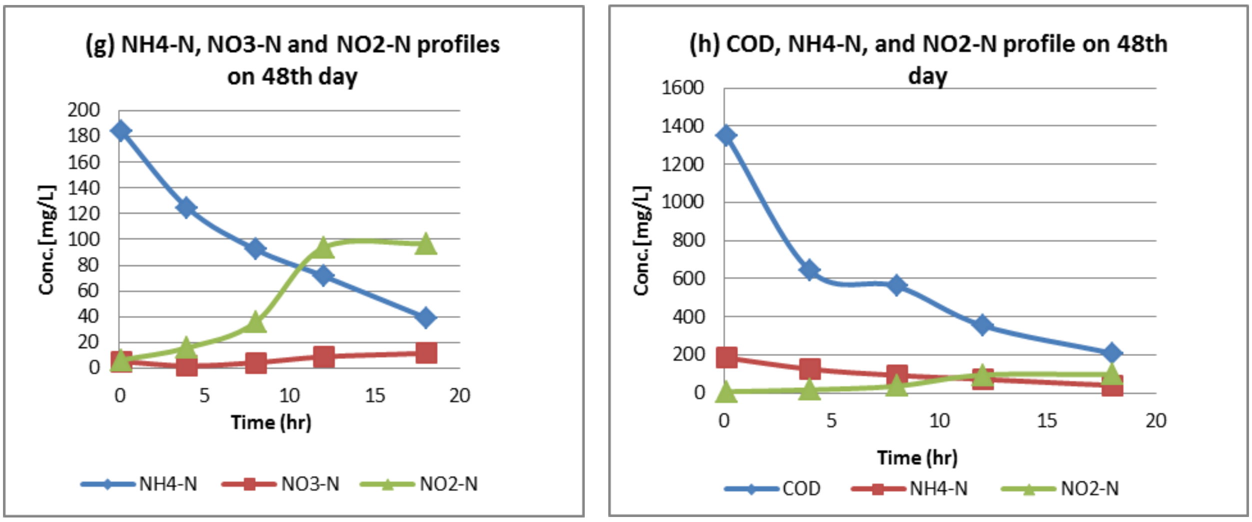


Figure 2: The reactor loading rates and effluent characteristics (a), the COD removal efficiency and initial mixed liquor and final effluent characteristics (b) , the NH4-N removal efficiency and initial mixed liquor and final effluent NH4-N(c), the initial and effluent total nitrogen and the total nitrogen removal (d), The reactor NO2-N and NO3 profile on day 47 (e), The reactor NO2-N and NO3 profile on day 52 (f), the reactor NH4-N(g), NO2-N and NO3-N profile on day 48 (h), the reactor COD, NH4-N(g), NO2-N and NO3-N profile on day 52 (h)

CONCLUSION

Simultaneous removal of organic carbon and nitrogen was possible from synthetic tannery wastewater using sequencing batch airlift reactor. The startup time for COD removal was very short while that for ammonia removal was higher and the study shows a start up time of 30 days for the case of synthetic tannery wastewater compositions used in this study. Operating the SBAR at low SRT (10d) shows partial nitrification to nitrite and the total nitrogen removal was higher when the ammonia conversation was high.

ACKNOWLEDGEMENT

The author sincerely thanks the Leather Industry Development Institute (LIDI), Government of Ethiopia, Addis Ababa, for full financial support for his Ph.D. studies under Twinning Program between Leather Industry Development Institute (LIDI), Addis Ababa University (AAU) and CSIR-Central Leather Research Institute (CLRI).

REFERENCES

Abdallh, M. N. and H. WalidSayedAbdelhalim (2016). "Biological Treatment of Leather Tanneries Wastewater Effluent-Bench Scale Modeling." International Journal of Engineering Science **2271**.

Anjali, G. and P. Sabumon (2014). "Unprecedented development of anammox in presence of organic carbon using seed biomass from a tannery Common Effluent Treatment Plant (CETP)." Bioresource Technology **153**: 30-38.

APHA, A. (1998). "WEF, Standard methods for water and wastewater examination." American Public Health Association **21**.

Bosnic, M., J. Buljan, et al. (2000). "Pollutants in tannery effluents." UNIDO, Vienna, Rev.

Dohare, D. and N. Kesharwani (2014). "A Review on Wastewater Treatment Using Sequential Batchreactor." International Journal of Scientific and Technology(3): 1135-1138.

Eckenfelder, W., Y. Argaman, et al. (1991). "Principles of biological and physical/chemical nitrogen removal." Phosphorus and nitrogen removal from municipal wastewater: principles and practice (2nd edition). 3-42.

Faouzi, M., M. Merzouki, et al. (2013). "Contribution to optimize the biological treatment of synthetic tannery effluent by the sequencing batch reactor." Journal of Materials and Environmental Science **4**(4): 532-541.

Ganesh, R., P. Sousbie, et al. (2015). "Nitrification and denitrification characteristics in a sequencing batch reactor treating tannery wastewater." Clean Technologies and Environmental Policy **17**(3): 735-745.

Gerardi, M. H. (2003). Nitrification and denitrification in the activated sludge process, John Wiley & Sons.

Henze, M. (2008). Biological wastewater treatment: principles, modelling and design, IWA publishing.

Kim, D.-J. and D. Seo (2006). "Selective enrichment and granulation of ammonia oxidizers in a sequencing batch airlift reactor." Process Biochemistry **41**(5): 1055-1062.

Leta, S., F. Assefa, et al. (2004). "Biological nitrogen and organic matter removal from tannery wastewater in pilot plant operations in Ethiopia." Applied Microbiology and Biotechnology **66**(3): 333-339.

Münch, E. V., P. Lant, et al. (1996). "Simultaneous nitrification and denitrification in bench-scale sequencing batch reactors." Water Research **30**(2): 277-284.

ECT O-33

MICROBIAL FUEL CELL A NOVEL TECHNOLOGY FOR EFFLUENT TREATMENT AND ELECTRICAL ENERGY GENERATION

Divyalakshmi P*, C Lajapathi Rai

*Chemical Engineering Division, CSIR – Central Leather Research Institute, Adyar, Chennai- 600 020, India *Email: divya.lakshmi90@gmail.com*

Chemical Engineering Division & Chemical and Biological Pilot Plants, CSIR – Central Leather Research Institute, Adyar, Chennai – 600 020, India Email: clrai@hotmail.com

MFC is one of the developing technologies to tap electrical energy from tannery effluent treatment plant without affecting its treatment efficiency. In the present study, a vertical MFC reactor has been used in order to simulate the real effluent plant which is partitioned into two sections by proton exchange membrane. The upper portion acts as an air cathode and the bottom part contains anaerobic biomass which acts as an anode, where the effluent gets treated. During treatment the organics present in the effluent gets degraded by sludge biomass and as a consequence electrons and protons are generated along with by-products. Electrons move through external circuit whereas protons migrate towards proton exchange membrane thereby generating a potential difference which is used for power generation.

Experimental studies were conducted in order to enhance the effluent treatment process and power generation. Increasing the surface area of the electrode enhances only the power generation whereas when the anaerobic biomass is subjected to diligent mechanical disintegration along with increased electrode surface area, enhancement of both effluent treatment and power generation were observed.

In control studies the maximum open circuit potential was 0.5 V with current generation of 0.1 mA (at 10Ω), Coulombic and COD removal efficiencies were 4 and 76% respectively. In the experimental reactors, where the surface area of the electrode alone was increased (3.5 times), an enhancement of 22% in voltage, 13% in current and 3.5% in power were observed. The Coulombic and COD removal efficiencies were 5.2 and 86% respectively. In this study a new approach was adopted by introducing a diligent mechanical disintegration in order to enhance the power generation as well as coulombic and COD removal efficiencies. Thus, enhancement in potential difference of 53%, current 28% and power 15% were achieved, and as a consequence the Coulombic and COD removal efficiencies were significantly improved to 13 and 90% respectively. At this stage it can be concluded that, by increasing the surface area of the electrode and the microbial maintenance energy requirements (i.e., by diligent mechanical disintegration) an enhancement in overall performances of MFC can be achieved.

Keywords: Tannery effluent treatment, MFC, Current generation, COD removal, Coulombic efficiency, mechanical disintegration

INTRODUCTION

Microbial Fuel Cell (MFC) is one of the emerging technologies to tap bio-electrical energy from effluent treatment without affecting the efficacy of the treatment plant. One of the biological methods i.e. activated sludge processes is being followed to treat industrial effluents. The NEERI report (1997) stated that processing of 1 kg of leather can approximately generate 40 L of effluent. As a result tanning industry generates nearly 15 million litres of effluent for processing 1 ton of raw skins and hides. New technologies are being introduced for tanning process in order to reduce water consumption (Silambarasan et al. 2015) however the effluent generations are not fully avoided. These effluents were collectively treated at common effluent treatment plant (CETP). During treatment, the effluent organics were degraded by microorganisms (i.e. biomass) and generates CO_2, electrons and protons. These electrons and protons are utilized in such a way for the generation of electricity through MFC (Gupta et al., 2011, Rahimnajad et al., 2015). MFCs were classified into two types based on electron transportation. The microorganisms that are electrochemically inactive, requires mediators such as thionine, methyl viologen, humic acid etc., to transfer electrons from microbial cell to electrode (Pandey et al., 2011). The organisms which are electrochemically active, does not require any mediators and the transfer of electron taken directly from microbial cell to fuel cell electrodes (Chang et al., 2006). However, the mediators are expensive and even toxic to microorganisms if the concentration is more than the threshold limit. Rabaey et al., (2005) identified that anodophilic consortium are able to transfer electron directly from microbial cell to electrode. Park and Zeikus, 2002 stated that mixed culture generates six times higher power than axenic. Gil et al., 2003 reported that in microbial fuel cell the rate limiting steps are the oxidation of fuel, electron transfer from microbial cells to electrode, electric load, and proton transfer into cathode section, oxygen supply and reduction at cathode. In the past, studies are carried out mostly by dual chamber MFCs separated by proton exchange material/salt bridge with the specific microbes and synthetic effluent for power generation. One part is considered as anode in which microbes and effluent were presented, and in cathode oxidizing agents such as potassium ferric cyanide, permanganate, potassium persulphate was added. Rabaey et al., (2003) uses Geobacteriaceae with glucose as fuel and generates maximum power density of 3.2 W/m^2. Similarly Deval and Dikshit, (2013) studied with salmonella species with sodium acetate as fuel, and Bacillus megaterium with artificial wastewater and distillery wastewater as fuels which generated maximum potential of 0.491V and 74mV respectively.

Studies show that single chamber up flow and tubular MFC reactors were also used to treat effluent using air cathode. Among all, MFCs with air cathode is most attractive and cost effective method avoiding usage of toxic oxidizing agents. Liu and Logan (2004) studied air cathode single chamber MFC for electricity generation both with and without proton exchange membrane. The cultured bacteria from wastewater were used as inoculum, glucose and domestic wastewater as substrate and thus achieved maximum power density of 262 mW/m^2 with coulombic efficiency of 40-55%.

At this point it may be stated that most of the MFC work carried out earlier were dual chamber with specific microorganism to treat synthetic wastewater using oxidizing agents in cathode section. However in the present work air cathode was used in vertical MFC reactor to treat tannery effluent using anaerobic biomass for energy generation. In addition new techniques are adopted to enhance the overall MFC performance.

MATERIALS AND METHODS

Anaerobic biomass and Tannery effluent

In the present study heterotrophic anaerobic biomass was used as microbial source collected from biomethanation plant, Chennai and the tannery effluent collected from CETP, Chennai was used as organic source. In order to prevent any further degradation sludge and effluent samples were refrigerated at 4 ˚C. The Initial characteristics of biomass and effluent are tabulated in Table. 1.

MFC Reactor and operation

Identical perspex MFC reactors were fabricated with the working volume of 1.2 L, equally divided into two halves by proton exchange material. The bottom is anode part where anaerobic biomass is presented and the effluent is pumped from the bottom using peristaltic pump for treatment. The upper part is air cathode and the electrodes were graphite rod with identical in geometry. A standard copper wire was used to connect the electrodes and the power generated during the studies was stored in data acquisition system. The schematic representation of MFC reactor set up is given in Fig 1.

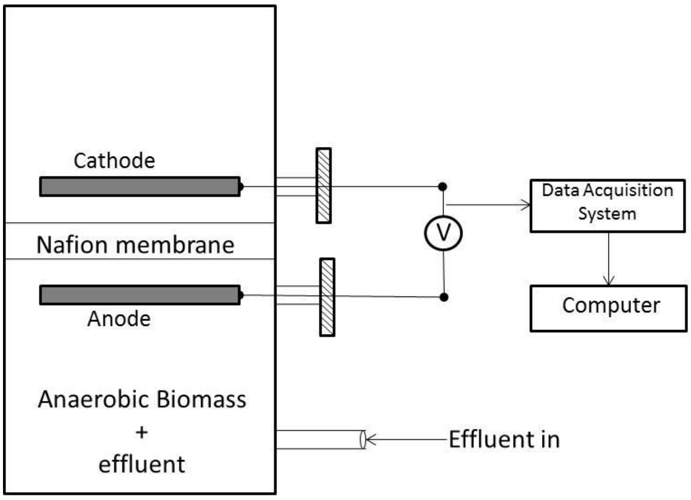


Fig 1. Lab scale MFC reactor

Table. 1 Characteristics of anaerobic biomass and tannery effluent

S. No.	Parameters	Anaerobic Biomass	Tannery Effluent
1.	pH	7.65	7.42
2.	TS (mg/L)	38.45	--
3.	VS (mg/L)	22.32	--
4.	COD (mg/L)	1240	6850

Three different experiments were carried out namely C1, E1 and E2. Experiment C1 was considered as control study in which graphite rods were used as electrodes with the surface area of 13.3 cm^2 each. In E1 the surface area of the electrodes was increased by 3 times (42 cm^2) that of control whereas in E2 the anaerobic biomass was subjected to diligent mechanical disruption in addition to increased electrode surface area of 42 cm^2

Disruption of anaerobic biomass

Ultrasonic homogenizer (UH) was chosen as disrupting device with the frequency of 20 kHz, model VCX 750, Sonics Vibra cell, USA. The degree of disruption was determined by soluble COD measurements with the following expression.

$$DD_{COD}(\%) = \frac{COD_t - COD_i}{COD_a - COD_i} \times 100 \qquad (1)$$

Where CODtis SCOD of treated sludge sample in mg/L; CODiis SCOD of initial sludge samplein mg/L; CODais SCOD of alkali digested sludge in mg/L.

Energy supplied to treat anaerobic biomass by ultrasonic homogenizer was calculated by the following expression.

$$E_{SE}\left(kJ/kg\right) = \frac{P \times t}{V \times TS} \qquad (2)$$

Where E_{SE} is Specific energy input in kJ/kg; P is Power in kW; TS is Total solids in sludge sample in kg/L; t is Disintegration time in sec; V is Volume of treated sludge in L.

Analysis

Standard methods for examination of water and wastewater (APHA) are used to characterize and analyze the anaerobic biomass and effluent respectively. Total and volatile solids in anaerobic biomass were determined by 2540 G method. The pH in the system was measured using ELICO LI120 pH meter. Chemical Oxygen Demand (COD) was determined by closed reflux titrimetric method (5220 C).

In order to calculate the current generated the Ohm’s law was used (i.e. V=IR), if external load and potential difference are known from the experiments. Similarly the power can be calculated by using the expression P=VI, Current and power densities were determined by surface area of the electrodes (current density = I/A, power density = P/A, where A is the surface area of anode electrode). The amount of organics degraded in the effluent was evaluated by COD removal efficiency and the coulombic efficiency can be calculated by the expression reported by Logan, 2008, which describes the conversion of effluent organics into electricity.

RESULTS AND DISCUSSION

Effect of surface area and pretreatment on cell voltage

Fig. 2 shows the voltage of MFC reactors operated at different conditions. It was observed that due to acclimatization of biomass to the tannery effluent, the potential increases slowly during startup time. As the retention time increases i.e. from 2 to 3 days the potential increases steadily and reaches the maximum. Thus by comparing with control studies both the experimental reactors shows higher voltage generation. In reactor E1, where the surface area of electrode was increased a maximum of 610 mV was generated due to more number of electrons transferred and increased surface area and thus the probability of electron capture by the electrodes are more. Similarly in reactor E2, in addition to increased electrode surface areas, diligent mechanical treatment was given to anaerobic biomass and thus disintegrates the microbial flocs so that more microbes will participate in degradation of organics in the effluent. Furthermore some of the microbes may get damaged during mechanical treatment thereby microbial maintenance energy got increased resulting enhanced degradation process.

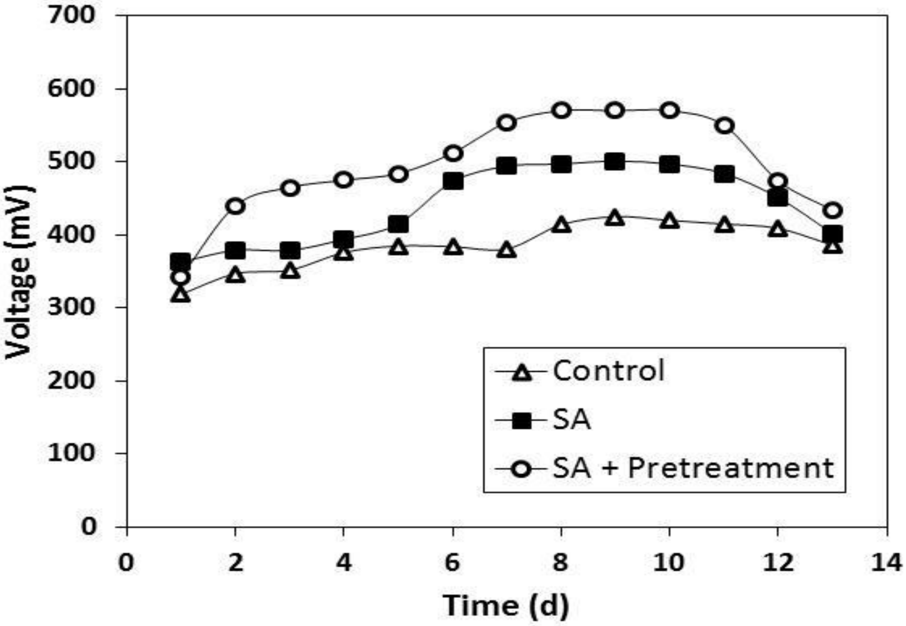


Fig 2. Voltage generation as a funtion of time

Effect of surface area and pretreatment on power generation

The power generation with the resisitance of 1000 Ω in experimental reactors were observed to be higher than control studies. The reasons may be stated as due to large surface area of anode, presence of exoelectogenic microbes in biomass and low anodic potential. Thus the power and current densities were calculated and shown in Fig 3. The Maximum power density of 20.2 mW/m^2 was achieved in the reactor E2 where both surafce area and mechanical treatement effects were introduced.

It was observed from past studies that power density for complex eefluents are lower than the specific substrates such as acetate, glucose, sucrose,etc. which are easily soluble and assimilated by microorganisms. Effluent from industries though it contains organic substances that are complex in nature which are not readily available for microorganisms. Early studies (Rahimnejad et al. 2015) reported that complex effluents such as starch, anaerobic sediments and domestic shows the power densities of 19, 20 and 28 mW/m^2. In tannery effluent it shows even lower than the reported values which may due to presence of suspended solids, sulphates, phenol, oil and grease which are low biodegradability in nature. Upon comparing with control studies, the experimental recators E1 and E2 shows enhancement upto 31.5 and 77 % respectively.

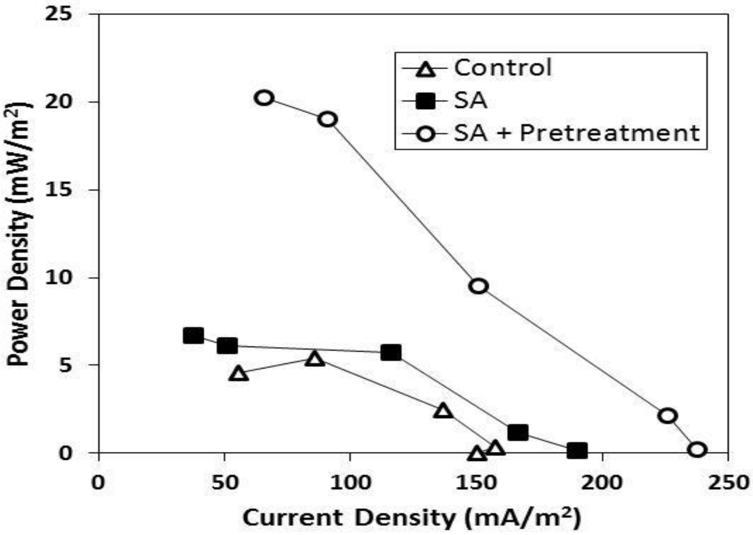


Fig 3. Power density as a function of current density for different external resistance

Determination of internal resistance

Internal resistance can be determined by using polarization slope method i.e. by plotting potential versus current and the slope yields the internal resistance. The comparison of the reactors show that in control study higher internal resistance was observed as 631 Ω. It may be related to slow movement of protons towards the cathode part whereas in experimental the internal resistances were observed as 397.4 and 259.1 Ω for E1 and E2 respectively. At this stage it may be concluded that the reduction in internal resistance was mainly due to increased surface areas of electrode and mechanical treatment and thus achieved for E1 and E2 as 36% and 58% respectively.

COD Removal and Coulombic Efficiency

The amount of organics removed during effluent treatment are calculated by COD removal efficiency. From the studies it was observed that COD removal for all reactors were 76, 86 and 90% respectively. Compare to control, enhanced in organics removal of 18 and 13% were obtained in reactors E1 and E2. The coulombic efficiency as function of current density for all reactors are given in Fig. 4. The coulombic efficiencies of 4, 5.2 and 13% were observed for all reactors. Comparison shows maximum enhancement of 69% for the reactor E2 was observed where the effects of surface area and mechanical treatments were introduced whereas in reactor E1 an enahancemnt of 55% was observed. The Current density, Power density, COD removal efficiency and coulombic efficiency of all reactors were tabulated in Table 2. The reason for lower coulombic efficiency for all reactors may be due to electrons loss in the alternate electron acceptors such as sulfate and nitrate presented in effluent.

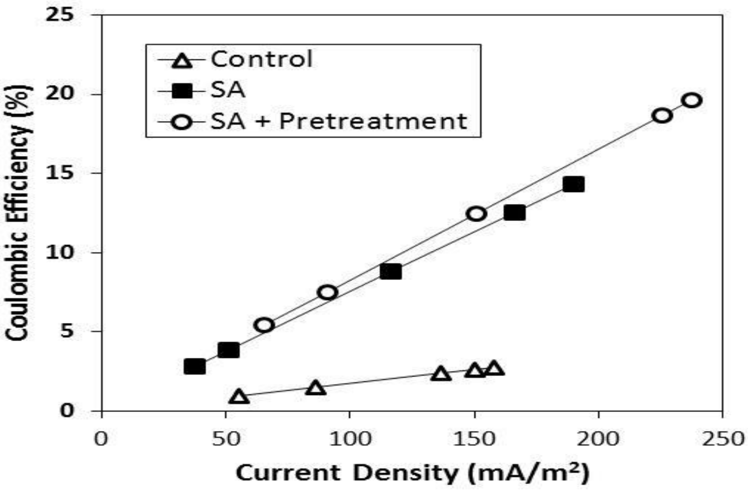


Fig 4. Coulombic efficiency as a funtion of current density

Table 2. Current density, Power density, COD removal efficiency and coulombic efficiency for different reactors

Experiments	**Current Density (mA/m^2)**	**Power Density (mW/m^2)**	**COD Removal Efficiency (%)**	**Coulombic efficiency (%)**
Control	37.7	4.6	76	4
SA (E1)	55.5	6.7	86	5.2
SA + Pretreatment (E2)	65.5	20.2	90	13

Conclusions

In the present MFC studies tannery effluent was used as a fuel for power generation. In order to enhance the MFC performance the effect of increasing the electrode surface area was studied. Thus an enhancement of 22% in potential, 13% in current, Coulombic and COD removal efficiencies were observed as 5.2 and 86%. Further, introducing diligent mechanical treatment on biomass along with increased surface area, an additional enhancement was observed as 53% in potential, 28% in current were achieved and as a consequence Coulombic and COD removal efficiencies were also increased to 13 and 90% respectively. Though the columbic efficiency in this study appears to be still lower, the main reason is the presence of sulphates, and nitrates in the tannery effluent which acts as an alternate electron acceptor affecting the MFC power generation. In order to alleviate the problem associated with MFC performance, segregation of tanning process effluent or separate treatment process to make the effluent free from alternate electron acceptors for better power generation.

REFERENCES

1. Wastewater management in cluster of Tanneries in Tamil Nadu, NEERI Report, 1997.
2. Silambarasan S, Aravindhan R, Raghava Rao J, Thanikaivelan P, Waterless tanning: chrome tanning in ethanol and its derivatives. **RSC Adv.**, 2015, **5**, 66815-66823.
3. Gupta G, Sikarwar B, Vasudevan V, Boopathi M, Kumar O, Singh B, Vijayaraghavan R, Microbial fuel cell technology: A review on electricity generation.J.Cell Tissue Res., 2011, **11**, 2631-2654.

4. Rahimnejad M, Ahami A, Darvari S, Zirepour A, Oh S, Microbial fuel cell as new technology for bioelectricity generation: A review, Alexandria Eng. J., 2015, **54**, 745-756.

5. Pandey B K, Mishra V, Agrawal S, Production of bio-electricity during wastewater treatment using a single chamber microbial fuel cell. Int. J. Eng. Sci.Technol., 2011, **3**,42-47.

6. Chang I-S, HyunsooM, Orianna Bretschger, Jae Kyung Jang, Ho Il Park, Kenneth H. Nealson, Byung Hong Kim (2006) Electrochemically Active Bacteria (EAB) and Mediator-Less Microbial Fuel Cells, J. Microbiol. Biotechn., **16**,163-177.

7. Rabaey K, Verstraete W, Microbial fuel cells: novel biotechnology for energy generation.Trends Biotechnol., 2005, **23**, 291-298.

8. Park D H,Zeikus J G, Impact of electrode composition onelectricity generation in a single-compartment fuel cell usingShewanellaputrefaciens. Appl. Microbiol. Biotechnol., 2002, **59**, 58-61.

9. Gil GC, Chang I-S, Kim B H, Kim M, Jang J-K, Park H S, Kim H Y, Operational parameters affecting the performanceof a mediator- less microbial fuel cell. Biosens.Bioelectron., 2003, **18**,327–334.

10. Rabaey K, Lissens G, Siciliano S D, Verstraete W, A microbial fuel cell capable of converting glucose to electricity at high rate and efficiency. Biotechnol. lett., 2003,**25**, 1531-1535.

11. Deval A,Dikshit A K, Construction, Working and Standardization of microbial fuel cell. APCBEE Procedia, 2013,**5**, 59-63.

12. Liu H, Logan B E, Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. Envir. Sci. Technol., 2004,**38**, 4040-4046.

13. Vikram M, Sharpudin J Int. J.Eng. Sci. Res. Technol, 2016, **5**, 166- 174.

14. Ryu, E, Yeon, M, Kim, Lee S J, Characterization of microbial fuel cells enriched using Cr (VI) – Containing Sludge. J. Microbiol.Biotechn., 2011, **21**, 187-191.

15. APHA.Standard methods for the examination of water and wastewater.American Public Health Association, Washington DC, 1998.

16. Logan B. E.Microbial fuel cells, John Wiley & Sons, Inc., Hoboken, New Jersey, 2008.

INNOVATIVE ENVIRONMENTAL TECHNOLOGIES INCLUDING WATER RECOVERY FOR REUSE FROM TANNERY AND INDUSTRIAL WASTEWATER – INDIAN AND ASIAN SCENARIO

S. Rajamani

Chairman - Asian International Union of Environment (AIUE) Commission,
Old No.18, New No.45, First Street, South Beach Avenue,
MRC Nagar, Chennai – 600 028, India E-mail: dr.s.rajamani@gmail.com

Environmental challenges due to depletion of quality water resources and increase in salinity, it has become necessary to control Total Dissolved Solids (TDS) in the treated effluent with water recovery wherever feasible. Adoption of special membrane system has been engineered in many individual and Common Effluent Treatment Plants (CETPs) in India, China and other leather producing countries. The sustainability of saline reject management is one of the major challenges.

Conventional tannery wastewater treatment systems include physiochemical and biological treatment to reduce Chromium, BOD, COD and Suspended Solids. To tackle treated effluent with TDS in the rage of 10000 to 30000mg/l, multiple stage high pressure membrane units have been designed and implemented for recovery of water. To reduce the chemical usage and sludge generation in the tertiary treatment, Membrane Bio-Reactor (MBR) has been adopted which replace secondary clarifier and sophisticated tertiary treatment units such as Reactive Clarifier, Ultra-filtration (UF), etc. Commercial scale high-tech membrane systems have been implemented in many locations for the capacities ranging from 500 to 10000m^3/day.

This paper deals with the recent developments on the environmental protection techniques in tannery wastewater treatment with focus on water-recovery for reuse, salt recovery, marine disposal of saline reject with proper bio-control system, etc. Details of applied innovative treatment technologies are provided in this novel technical paper. Sustainability of the Asian Leather Sector due to enforcement of new and stringent environmental regulations is also dealt in this paper.

Keywords: Effluent Treatment System, Environment, Sustainability, Water Recovery.

1. INTRODUCTION

Annual leather process in Asian Countries is estimated at 8 to 10 million tons of hides and skins which is more than 50% of the estimated World leather production of about 16 million tons per year. Wastewater discharged from world tannery sector is about 600million m^3/annum. The tanneries in Asian countries including India, China, Vietnam, etc. discharge more than 350 million m^3 of wastewater per annum.

The conventional physiochemical and biological treatment systems are designed and implemented only to reduce Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Suspended

Solids (SS), Heavy metals etc. and not TDS and salinity which are mainly contributed by chlorides, hardness and sulphates. Due to inherent quality of wastewater from tanning industry, the treatment plants are unable to meet the prescribed standards in terms of TDS, chlorides in salinity in the treated effluent.

There is not much scope in mixing the treated tannery effluent with domestic sewage to achieve the TDS level in many locations in Asia in the absence of organized sewage treatment plants of required capacity. Many polluting industries including tanneries are located in the land locked areas and there are constraints to discharge the treated effluent with high TDS in the Sea.

The TDS limit is being enforced in India and other parts of the World depending upon the final mode of disposal. In addition to the removal of TDS in the treated effluent, it is necessary to recover water for reuse to meet the challenge of water shortage. In many states in India, the pollution control authorities insist on water recovery integrated with Zero Liquid Discharge (ZLD) system. However, the achievement of Zero Liquid Discharge concept has got many technical challenges in addition to the application of various types of membrane systems. Management of the concentrated saline stream treatment by adopting energy intensive evaporation system seems to be one of the major issues in land locked areas.

This technical paper deals with the recent developments on the environmental protection techniques in including water recovery from water discharged from tanneries and other industrial waste water treatment with focus on sludge reduction water recovery for reuse and salt recovery, marine disposal of saline reject with proper treatment and guard, etc. Case studies of major projects implemented in India, Spain, China, etc. and saline reject disposal coastal zones are covered in the novel technical paper.

2. IMPROVED TREATMENT SYSTEM FOR SLUDGE REDUCTION, WATER RECOVERY & TDS MANAGEMENT

Due to inherent quality of industrial wastewater such as textile dyeing units, tanneries etc., the conventional treatment plants are unable to meet the prescribed TDS level of 2100 mg/l in the treated effluent. In addition to TDS management the control of volatile solids in hazardous category sludge is also becoming a necessary.

There is not much scope in mixing the treated industrial effluent with domestic sewage to achieve the TDS level in many locations in the absence of organized sewage treatment plants of required capacity. Many polluting industries are located in the land locked areas and there are constraints to discharge the treated effluent with high TDS in the sea.

The TDS limit is being enforced in many parts of the world depending upon the final mode of disposal. In addition to the removal of TDS in the treated effluent, it is necessary to recover water for reuse to meet the challenge of water shortage. In many states in India the pollution control authorities insist on water recovery integrated with Zero Liquid Discharge (ZLD) system.

For control of sludge and recovery of quality water from wastewater, the required treatment steps are (i) Chrome recovery and other in process control including cleaner production (ii) Conventional physiochemical and biological effluent treatment systems to reduce BOD, COD, SS etc. and (iii) Tertiary treatment systems including, micro-filter, low pressure membrane units such as ultrafiltration etc., before the application of single or multiple stage Reverse Osmosis (RO) system. A special treatment process for recovery of water from waste water is given in Figure 1.

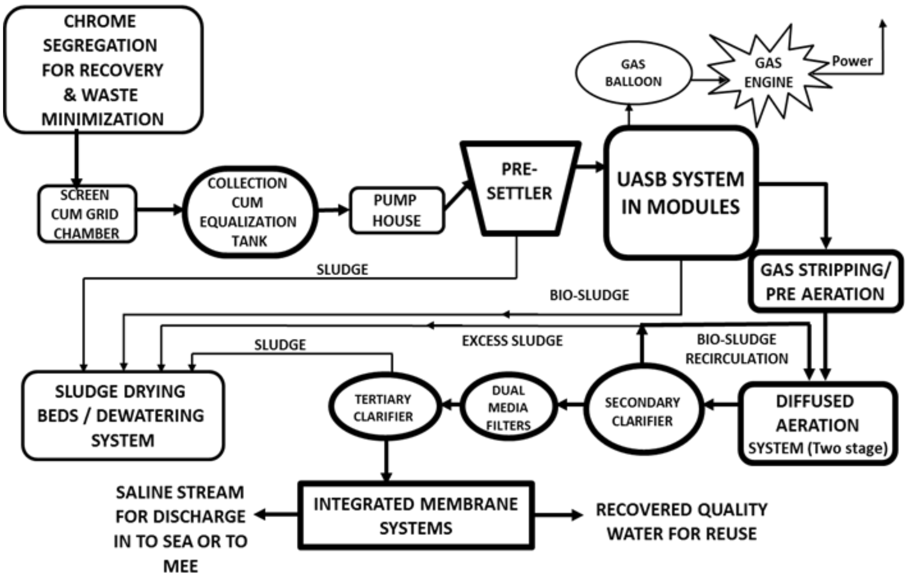


Fig. 1 - Process Flow Diagram for Tannery Waste Treatment & Integrated Saline Management – New and First of its kind

After primary and secondary treatment units, Reactive Clarifier, Dual Media Filter, Micro Filter, Ultra-Filter (UF) are installed prior to RO system for recovery of water.

The number of stages and types of RO system are based upon the TDS concentration in the feed water, estimated percentage of quality water recovery and reduction in volume of saline reject. High pressure Sea water membrane is adopted for handling treated effluent with TDS concentration more than 10,000 mg/l. The quality water recovery rate could be achieved to the level of 70 to 90% depending upon the feed water TDS level, type and stages of membrane system etc. In addition to recovery and reuse of quality water by the industry, the additional benefits are savings in chemical usage in the tanning process and reduction in pollution load in the effluent. The reject saline stream from RO system needs to be managed by adopting the options of forced / thermal evaporation system or disposal into Sea wherever feasible with suitable control.

Fig. 2 - Amiad Filter & Ultra-filter (UF)

Many full scale membrane systems have been installed for recovery of water from domestic and tannery wastewater with capacities ranging from 100 to 20000m^3/day.

3. MEMBRANE BIO-REACTOR (MBR) INTEGRATED WITH RO SYSTEM

Membrane Bio Reactor (MBR) system is commonly adopted in many countries to remove the residual BOD, suspended solids / coliform, etc. from the effluent. After treatment with MBR, the water is applied through RO system for removal of TDS and salinity to get drinkable quality water with TDS less than 500mg/l. A Common Effluent Treatment Plant (CETP) in Spain with MBR and RO system for water recovery was established in 2005. Recent times many CETPs in India have adopted MBR and other membrane system for water recovery and reuse from the tannery effluent. After MBR / UF treatment, the suspended solids and BOD values in the effluent are below detectable level and taken for treatment with RO system for recovery of water after the removal of TDS and salinity.

In China also water is becoming a scarce commodity in many locations. Expansion of high water consuming industries is allowed only if they are provided with water recovery system in the effluent treatment plants. To recover water from the tannery wastewater, submerged MBR linked with activated biological treatment is provided in the first stage. Following MBR system an RO plant in “Christmas Tree” configuration has been installed and operated at 12–16 bars. The RO plant produces about 70% permeate and 30% concentrate. The quality of the recovered water meets the drinking water standards. The saline water concentrate stream is further treated with Fenton process before disposal.

A view of the submersible MBR in one of the tannery effluent treatment plants in China is shown in Figure – 3.

Fig. 3 - Reverse Osmosis system following MBR / UF

The Nano Filtration (NF) is adopted for removal of colour and salts such as sulphates from the treated effluent after ultra filtration or MBR stage. Nano-filtration membranes are operated under low pressure with high yield of about 90%. Adopting NF will improve the efficiency of RO in water recovery and to decrease the volume of saline reject.

Multiple stage evaporators using thermal and electrical power have been installed for evaporation of the reject saline stream from RO system. However, there are many technical issues such as constrains in continuous operation of the system, meeting the required quality of the condensate water from the evaporator for reuse, management / utilization of the recovered salt with impurities etc., The capital and operational costs are also high. Further techno economical review and modified options are required on the sustainability of the system particularly in land locked areas.

4. MARINE DISPOSAL OF TREATED SALINE STREAMS FOR TDS MANAGEMENT

A novel technological development has been made for the drawl of Seawater of 30,000m^3/day from nearby Sea for the desalination plant integrated with a major leather complex in South India. Out of the total water quantity, freshwater of about 10,000m^3/day will be generated and the remaining 20,000m^3/day will be discharged into Bay of Bengal with special bio-control and dispersion system to safe guard the aquatic life. The leather complex will be using the freshwater generated by desalination plant for its process requirements and 9,000m^3/day wastewater will be treated, mixed with saline reject of the desalination plant, stored in a water tight pond for a capacity of about 10 days and discharged into the Sea by laying 5 km pipeline using high pressure HDPE pipe and special sprinkling system. The combined treated saline stream with a quantity of about 29,000m^3/day will be discharged once in a week under the overall control of environmental protection authorities.

With the support of many National Institutes and other organizations, model studies were carried out in finalizing the novel marine outfall. The spreading of an effluent cloud released in a marine environment is governed by advection caused by large scale water movements and diffusion caused by comparatively small scale random and irregular movements without causing any net transport of water. Hence, the important physical properties governing the rate of dilution of an effluent cloud in coastal waters are bathymetry, tides, currents, circulation and stratification.

A five port diffuser systems with 0.18 m diameter is planned with a jet velocity of 2.5 m/sec, for the release of treated effluents and reject water from the proposed desalination plant.

The Environmental Clearance (EC) and approval has been accorded by Government of India to this unique integrated project with water recovery using desalination process, tannery wastewater treatment, novel and safe saline reject disposal into Sea without affecting the marine life which is first of its kind in India.

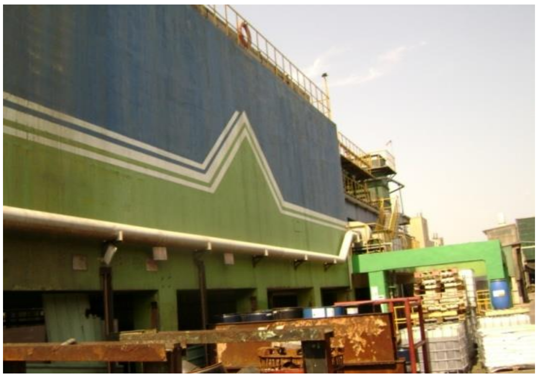
5. Technological developments in Asian and major leather producing countries

The recent developments in cleaner production and waste management in Asian and other major leather producing countries are given in Table 1.

Table 1 – Technological Developments in Environmental Protection

Country	Research & Technological Development
BANGLADESH	The main tannery cluster in Bangladesh is located in Dhaka city. Tanneries introduced cleaner technologies and chrome recovery system etc. with the support of UNIDO. The tanneries from the Dhaka city are being relocated in a newly developed industrial estate with Common Effluent Treatment Plant (CETP) of 30MLD capacity.
CHINA	Currently there are about 800 tanneries. Till now, about 13 CETPs are in operation, some more are under planning. Planned to reduce the volume of water usage and pollution load at source through cleaner production programme. The tanneries are permitted to expand the capacity without increase in the water usage. One of the major tanneries has implemented the MBR and RO system for water recovery and reuse.  **Fig. 4 - Submerged Membrane Bioreactor** As such there is no specific restriction on the Total Dissolved Solids (TDS) or salinity norms for the disposal of treated effluent. However meeting the BOD, COD norms for the saline streams from RO is one of the issues being addressed by new technological development. As a sustainability measure new licenses are given to tanneries with a processing capacity of more than 3000 tons /year of raw hides and skins.
INDIA	A biggest CETP in Asia with a capacity of 48,000m^3/day (48 MLD) for 450 tanneries is being planned with a budget of about 60 million USD in Kanpur city. Zero Liquid Discharge concepts by adopting membrane system for recovery of water from tannery effluent have been implemented in the South Indian tanneries at a cost of about 100 million USD. 

Country	Research & Technological Development
	Fig. 5 - UASB system with Bio-Energy generation from a CETP in India. Disposal of the saline stream from membrane units in land locked areas is one of the unresolved technical challenges. Treated effluent is mixed with treated domestic sewage and utilized for green development in some of the land locked areas. Decentralized secured landfill system linked with CETPs for leather sector had been implemented in many tannery clusters. (First of its kind in the World). R&D activities on bio processing are under progress.
ITALY	Total aerobic biological oxidation system without the use of chemical is adopted in major CETPs for reduction of COD and sludge generation. Thermal treatment of sludge, energy generation from volatile organic matter and overall sludge management are followed. Central chrome recovery and reuse system are being adopted in many locations.  **Fig. 6 – Extended Aerobic oxidation for sludge reduction in a CETP, Italy**
NEW ZEALAND	Enzymes and unhairing process is becoming more popular. Elimination of salting of skins by introducing chilling process in selected areas, Sulphide oxidation, pH & settleable solids control and discharge of effluent into public sewer system.
ROMANIA	R & D activities in Cleaner Production and Environmental Protection are being carried out in National Research and Development Institute for Textiles and Leather (INCDTP) / ICPI. Many co-operation programmes in association with COTANCE and other institutions are under progress in Bucharest, Romania. Media and Conferences are effectively used to promote the importance and image of leather industry and environment protection activities.

Country	Research & Technological Development
	 PROMOTIONAL ACTIVITIES TO IMPROVE IMAGE AND GROWTH OF PROFESSIONAL IN LEATHER AND EFFLUENT TREATMENT – EUROPE & ASIA Leather Production with Environmental control is my job Using Media and Conference to promote the importance and image of leather industry and environment protection activities ICAMS 2014 - ROMANIA **Fig. 7 – ICAMS 2016 – Romania**
RUSSIAN FEDERATION	Many institutions such as Department of Leather and Fur Technology. Water Recourses and Commodity Research, East Siberia State University of Technology and Management, Ulan-Ude, Russia and other industrial organizations promote technological development and environmental protection in leather and other industrial sector.  **Fig.8 – Environmental Protection - LAKE BAIKAL – SIBERIA** **25% of World's Quality Water – Preserved without Pollution**
TAIWAN	Currently there are about 50 tanneries in operation in Taiwan. The tanneries are having individual treatment plants with capacities ranging from 300 m^3–2000m^3/day. They adopt conventional physiochemical and biological treatment systems.  **Fig. 9 – Multistage roof top, aerobic biological treatment unit, Taiwan**

Country	Research & Technological Development
TURKEY	There are about 540 tanneries existing in 14 zones. Eight Common Effluent Treatment Plants (CETPs) have been established and are in operation. The biggest CETP with a capacity of 36,000m^3/day is in Tuzla near Istanbul. The other major tannery cluster is in Izmir with an integrated CETP. The tanneries had resettled in industrial zones. The treated effluent is disclosed in to sea for TDS management with special bio-control.  **Fig. 10 - CETP in Istanbul, Turkey with Sea discharge for TDS management** R&D activities on cleaner production and environmental protection are being continued in universities such as Ege University, Izmir etc. Sludge disposal is a major problem similar to other countries.

6. CONCLUSION

The leather production activities especially raw to semi-finishing process are being shifted from the developed nations such as United States, West European Countries, to Asian, North African and Latin American Countries. The major tanneries in leather producing Countries such as China, Italy, India, Russian Federation, etc. have to develop and adopt new environmental protection measures such as adoption membrane system, water recovery, etc. due to enforcement of stringent environmental regulations. The sustainability of the small-scale units is becoming a serious issue to meet the new environmental requirements. Major investments are being made for environmental protection and resettlement of tanneries from the urban areas to the industrial parks with common effluent treatment plants. New regulations and restrictions such as REACH on the use of certain chemicals, salinity and water recovery under zero discharge concepts, disposal/management of chrome containing sludge etc. envisage continued Research & Development activity. Innovative tanning processes which will greatly reduce the water and chemical usage and minimize solid waste generation are needed together with overall environmental planning and management.

7. ACKNOWLEDGEMENT

The contributions of Asian International Union Environment (AIUE) Commission and IUE Commission members from various countries, IULTCS, UNIDO and European Union are acknowledged. Special efforts and inputs from Mr. Ivan Kral, UNIDO, Ms.Catherine MONEY, Ms.Patricia CASEY, Prof.Dr.**Mariliz Gutterres,** Ms.Katia Fernanda Streit, Mr.Chen ZHANGUANG, Mr.Su CHAOYING, Mr.Liyuzhong, Mr.Thomas Yu, Mr.Vera Radnaeva, Mr.Gokhan Zengin, Ms.Eylem Kilic, Dr.Campbell Page, Mr.Jakov BULJAN, Dr.Wolfram SCHOLZ, Mr.Elton Hurlow, Dr.Shi Bi, Dr.MaJianzhong, Dr.Volkan

Candar, Prof.Altan AFSAR, Dr.Keiji Yoshimura, Mr.M.Aihara, Mr.Juan Manuel SALAZAR, Dr.Dietrich Tegtmeyer, Mr.Arnab Jha, Ms.Suliestiyah Wiryodiningrat, Dr.Luminita Albu, Mr.Gustavo Gonzalez, Mr.Y.K.Luthra, Mr.Goeff HOLMES, Mr.Dylan BALL, Dr.Mwinyikione Mwinyihija, Mr.Arnold Mulder, Mr.Mohammad Aslam Mia and other technical committee members are greatly acknowledged.

The support and contributions of European Union (EU), AIICA and Spanish Leather Chemists Association (SLCA) are greatly acknowledged. The contributions of Central Leather Research Institute (CLRI), China Leather Industry Association (CLIA), Taiwanese Leather Industry Association (TLIA), Indian Leather Technology Association (ILTA), Latin American Congress Federation of Leather Industry Chemists and Technicians (FLAQTIC), Japanese Association of Leather Technology (JALT), National Research and Development Institute for Textiles and Leather (INCDTP), Krishnapatnam International Leather Complex Private Ltd. (KPILC), Nellore, Andhra Pradesh, India and Leather & Footwear Research Institute (ICPI) other Leather Industry Associations and Common Effluent Treatment Plants (CETP) are acknowledged.

6. REFERENCES

1. S.Rajamani, Environmental update in Asian and European Leather Sector, Indian Leather – 2016
2. S.Rajamani - Improved Chromium Recovery System Integrated with Water Recovery for reuse in tanneries under Zero Discharge (ZLD) Concept, Leather Age - 2016
3. S.Rajamani - Environmental Protection Measures including recovery of water for reuse from tannery wastewater – Asian Scenario, Leather News India - 2016
4. S.Rajamani - Environmental challenges & Technological development in Asian Leather Sector – Leather Age - 2015
5. S.Rajamani, Adoption of membrane system for recovery of water from tannery effluent and TDS management, Indian Leather - 2015
6. S.Rajamani, Sustainable Environmental Protection System for tanning industry with viable sludge and saline stream management, Leather News India – 2014
7. Asian International Union of Environment (AIUE) Commission documents on Environmental protection –2014
8. S.Rajamani, Concept and guidelines for Environmental Footprint for World Leather Sector, Leather News India – 2013
9. S.Rajamani, Environmental update in Leather producing countries, Taiwan, Leather News India – 2012
10. S.Rajamani & Patricia Casey, Environmental update in Leather Producing Countries– Argentina, Leather News India – 2010
11. S.Rajamani, Chen Zhanguang, Zhang Shuhua, Su Chaoying– Environmental Update in Leather Producing Countries, China, Leather News India – 2010
12. LL.Milá, X. Doménec et al., Use of LCA in the procedure for the establishment of environmental criteria in the catalan ecolabel of leather – 2002

DIP O-35

NEW DIMENSIONS IN CHILDREN'S SHOES

**Md Sadiq*, Gautham G, Suresh Kumar D, Sreeram KJ, Das BN, Chandrasekaran Bangaru
Dayalan K**

and manufacturing support by

Bachi Shoes Limited, Sanghavi Shoes Accessories, Euro Shoe Components

Shoe & Product Design Centre, Director, CATERS, CSIR-Central Leather Research Institute, Sardar Patel Road, Adyar, Chennai 600020, INDIA.
Email: mdsadiq@hotmail.com; bhabendra@gmail.com; kdclri@gmail.com; dsureshkumar@live.com, kjsreeram@gmail.com, bchandru@gmail.com
6C, Malles Altius, Sholinganallur Perumbakkam Road, Chennai 600102; email: gauthamgk@gmail.com

The Children's feet grow at a rapid rate thus necessitating a frequent change in footwear to accommodate this foot growth. In order to provide correct fitting shoes for them it is essential to gather reliable foot dimensions of children which was done through a 'digital capture' of the foot images.

A novel method of 'cluster analysis' led us to compress the complete children's size range from Children Size 10 to Adult Size 3 into only 5 Groups which helped in optimizing the size range to be manufactured, accommodated the foot growth in children and also reduced the frequency of footwear change.

New features: The Children's (both Boys and Girls) foot dimensions were reliably captured through a unique '3D Digital Capture' of the foot images. An innovative Statistical technique of 'Cluster

Analysis' of the foot data captured, led us to compress the complete children's (both Boys and Girls) size range into only 5 Groups which helped in optimizing the size range to be manufactured, covered children having different foot sizes comfortably, accommodated the foot growth in children and also reduced the frequency of footwear change.

The New Lasts developed are only 'five' in number and cover the entire spectrum of existing sizes of Children's Feet as spelt out in the conventional sizing systems available. Thus, the new feature of our Lasts is that the number of sizes of 'Lasts' that would be required will be less but at the same time there would be no compromise on the 'comfortable fitting' of all Children in the age group studied.

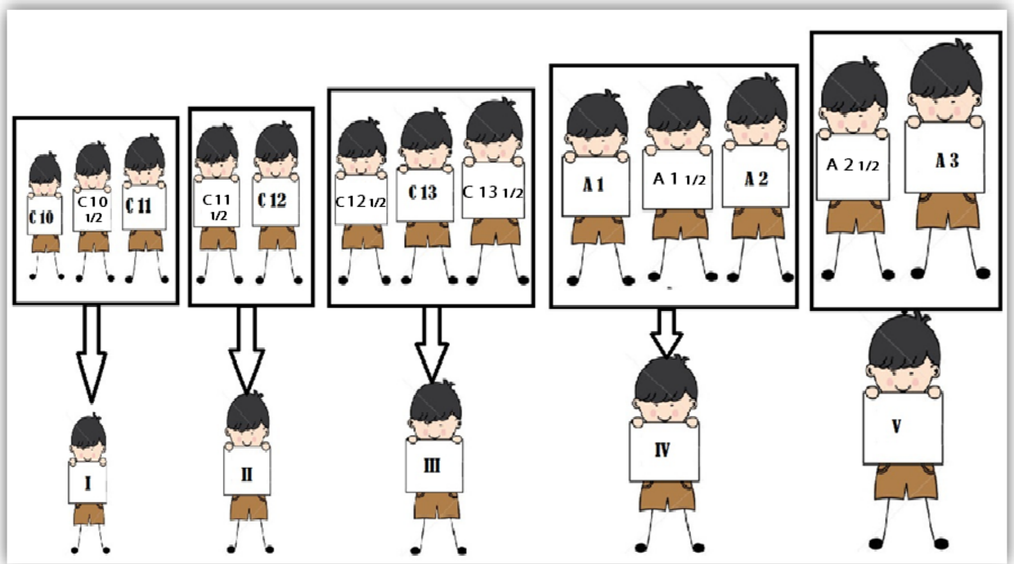
Thus, from the data derived it is clear that the new Dimensions derived by us give the Lasts developed for Children's Shoes in our Project a Wider Girth at the Ball and Instep points as well as a longer length which would help in accommodating the "growing feet" of the Children as well as provide them with a more comfortable shoe.

Children's Sizing Groups and Last parameters for each of these groups

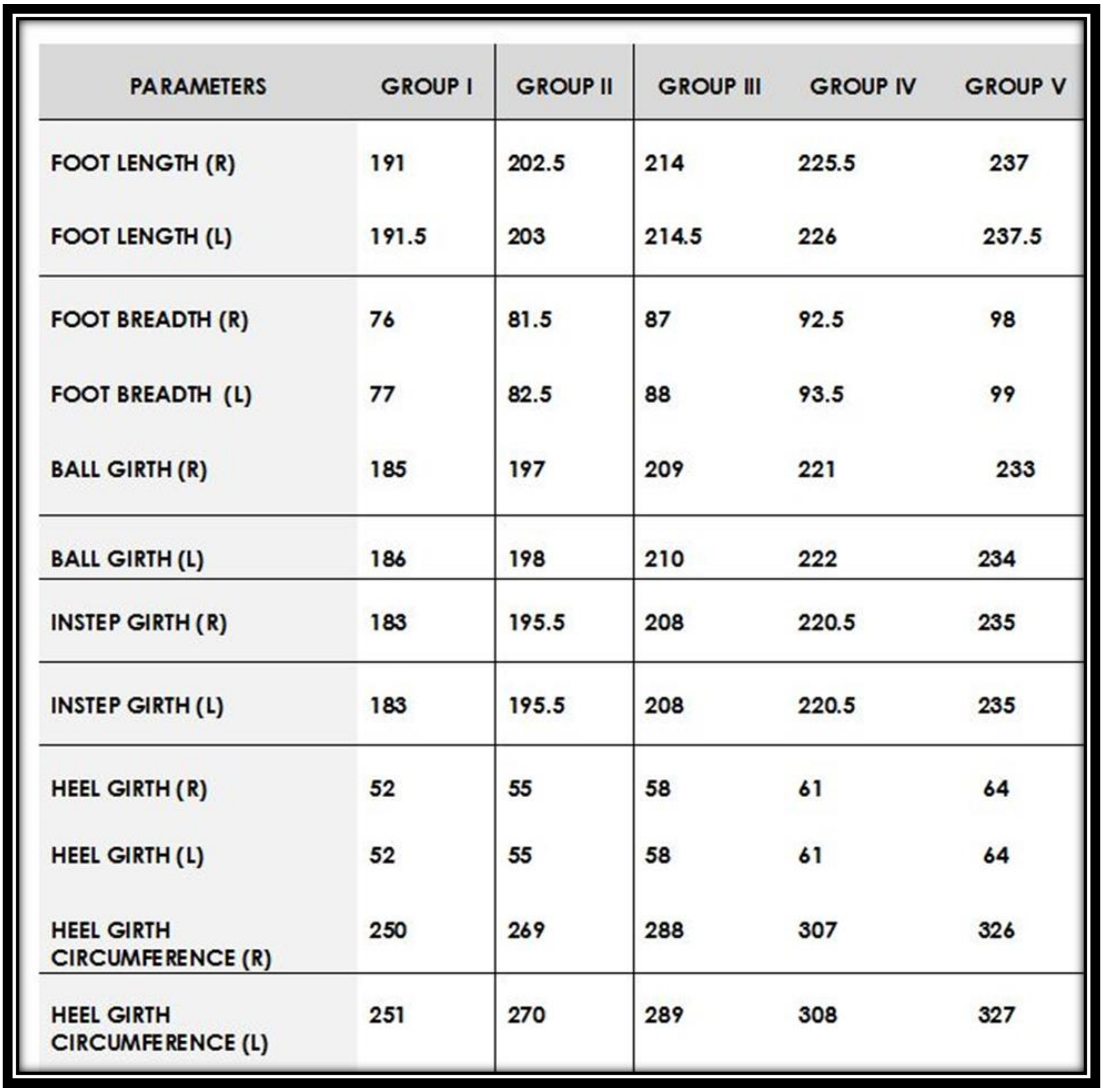
Since the Children's feet grow at a rapid rate thus mandating a frequent change in footwear to accommodate this foot growth, we felt that in order to provide correct fitting shoes for them it is essential to gather reliable foot dimensions of children and statistically analyze the data to derive the dimensions of the "lasts" which would fit the children – both Boys and Girls, perfectly providing for a Comfortable Footwear.

Accordingly, the Children's (both Boys and Girls) foot dimensions were reliably captured through a unique '3D Digital Capture' of the foot images. Sophisticated Statistical technique, led us to compress the foot data captured and resulted in the optimization of the complete children's (both Boys and Girls) size range into only 5 Groups which helped in minimizing the size range to be manufactured. The newly developed sizing system covered children having different foot sizes comfortably, accommodated the foot growth in children and also reduced the frequency of footwear change.

The new Dimensions gave the Lasts developed for Children's Shoes in our project a wider girth and a length which helped in accommodating the 'growing feet' of children and the fitting of the Children's Feet comfortably in the 'correct group' as opposed to the regular Size to Size standard increments available in the existing conventional 'lasts' for Children.



The derived LAST PARAMETERS are:



PARAMETERS	GROUP I	GROUP II	GROUP III	GROUP IV	GROUP V
FOOT LENGTH (R)	191	202.5	214	225.5	237
FOOT LENGTH (L)	191.5	203	214.5	226	237.5
FOOT BREADTH (R)	76	81.5	87	92.5	98
FOOT BREADTH (L)	77	82.5	88	93.5	99
BALL GIRTH (R)	185	197	209	221	233
BALL GIRTH (L)	186	198	210	222	234
INSTEP GIRTH (R)	183	195.5	208	220.5	235
INSTEP GIRTH (L)	183	195.5	208	220.5	235
HEEL GIRTH (R)	52	55	58	61	64
HEEL GIRTH (L)	52	55	58	61	64
HEEL GIRTH CIRCUMFERENCE (R)	250	269	288	307	326
HEEL GIRTH CIRCUMFERENCE (L)	251	270	289	308	327

Units in mm

The above 'Last Proportions' derived for the Children's Shoes are unique and novel.

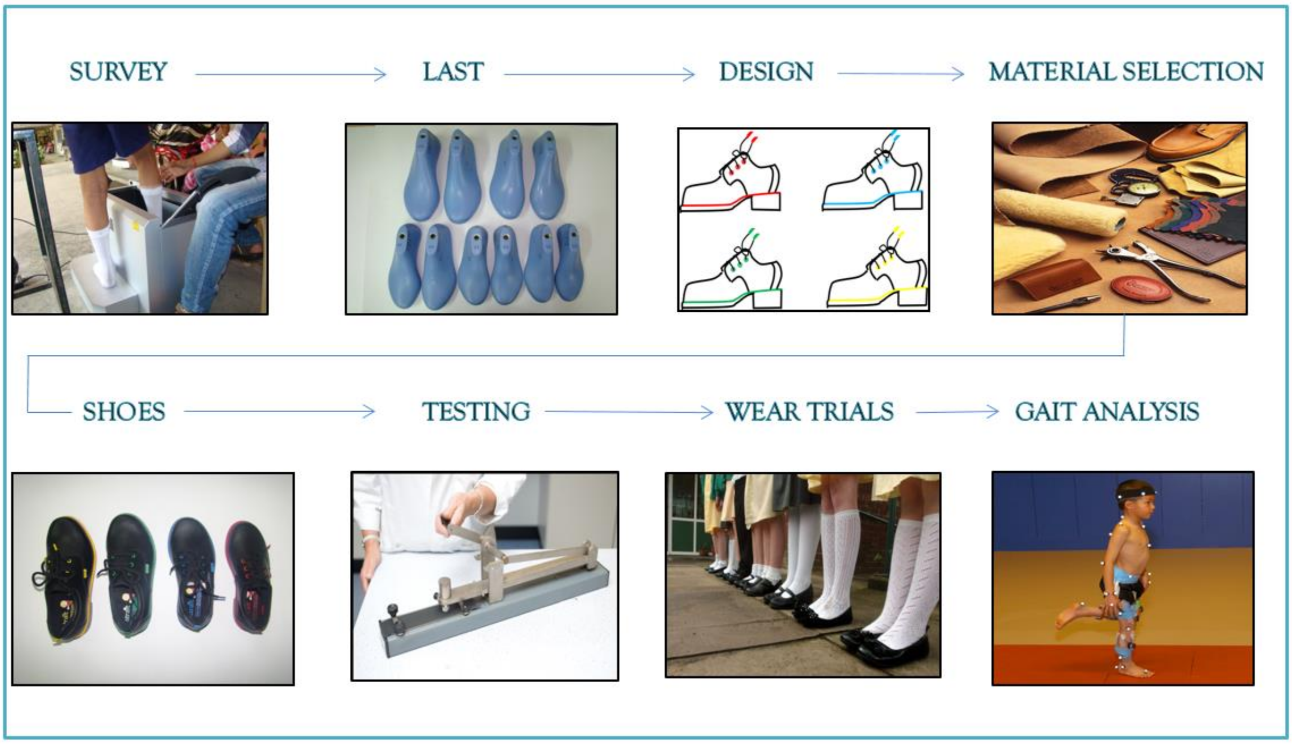
This would result in the easy accommodation of Children with different foot width in any of the Size groups and would also result in them reducing the frequency of footwear change as they would not outgrow their footwear for a long time as compared to conventional footwear made according to existing Sizing system which would certainly necessitate a higher frequency of footwear change as the children would outgrow their shoes faster.

The 'reduced' number of lasts also makes manufacturing easier and results in better productivity and faster turnaround times, if different styles have to be manufactured simultaneously.

Inventiveness: The values of Length, Ball Width, Ball Girth and Instep Girth dimensions that are used to model the Children's Lasts for both Boys and Girls are significantly different from the existing values of the Children's Lasts. The new Dimensions give the Lasts developed for Children's Shoes in our project a wider girth and a length which helps in accommodating the 'growing feet' of children and the fitting of the Children's Feet comfortably in the 'correct group' as opposed to the regular Size to Size standard increments available in the existing conventional 'lasts' for Children. This would result in the easy accommodation of Children with different foot width in any of the Size groups and would also result in them reducing the frequency of footwear change as they would not outgrow their footwear for a long time as compared to conventional footwear made according to existing Sizing system which would certainly necessitate a higher frequency of footwear change as the children would outgrow their shoes faster.

The 'reduced' number of lasts also makes manufacturing easier and results in better productivity and faster turnaround times, if different styles have to be manufactured simultaneously.

Industrial Applications: The 'LASTS' developed for the Children's Shoes would be used by 'Last' manufacturers to make multiple lasts and the Children's Footwear manufacturers would use these lasts to develop 'Children's Shoes' which would be of correct fit and comfortable for the Children wearing them.



Significant outcome

- Foot dimensions of the growing Children's feet captured through an **Anthropometric survey** using **Digital Image Capture Technique**
- **Statistically analysed** the captured Data for **'Cluster Grouping'** of foot sizes
- Modelled the derived **Last parameters**
- Incorporated **Children's Footwear Trends** in styling their shoes

- **Enhanced the comfort of the shoes** through an appropriate selection of components and accessories
- Fabricated special **fitting lasts**
- The styling was done to ensure the **‘comfort’** and **‘safety’** of the children.
- **Colours incorporated** in the styling of these shoes in harmony with the House to which these Children belong
- Shoes fabricated and the **wear trials** carried out for ‘Fit’ and ‘Comfort’ feedback
- Leather flag in House color printed with project name **(STRAIT).** Webbing tape in House color.
- Fabricated of **480 pairs** of footwear for children
- **Performance and Wear Evaluation** of fabricated footwear carried out
- **Gait Analysis** assessment for comfort after wear trials
- **Ready for commercialisation**

DIP O-36

STUDY OF DYNAMIC FOOT PROFILE OF PERSONS WITH DIABETES USING PLANTAR PRESSURE ANALYSIS

Sathish Babu.G*, Priyadharshini.R, Saraswathy.G, Das.B.N, and Vijay Viswanathan

Shoe and product development center, CSIR-CLRI, Adyar, Chennai 600020, India
Email: sathishbabuin@gmail.com
M.V.Hospital for Diabetes, No 4, West Mada Church Street, Royapuram, Chennai 600013, India
Email: drvijay@mvdiabetes.com

Foot and Gait-related problems are one of the consequences of diabetes mellitus due to changes in foot shape. To achieve uniform distribution of plantar pressure in the foot, there should be a match between foot profile and footwear profile. Foot outline and dynamic foot pressure distribution are essential elements that can influence footwear fitting. Very few studies have been conducted to study the dynamic plantar pressure of diabetic patients without any foot deformities. Earlier studies on plantar pressure distribution of persons with diabetes were done with static plantar pressure analysis data, and there is very little data available on dynamic plantar pressure analysis data for better fitting footwear development. This study aims to improve the design of therapeutic footwear for persons with diabetes neuropathy by analyzing dynamic plantar pressure profile of patients with diabetes without neuropathy (Group 1) and patients with diabetic neuropathy without any foot deformity (Group 2) and the data was compared with healthy subjects with normal foot profile (Control group). The plantar pressure analysis was performed using HR-Mat plantar pressure analyzer, P-walk BTS bioengineering, Italy. The results indicated that the dynamic plantar pressure in the Medial Heel (MH) was increased in both the group Diabetic and Diabetic neuropathy. The Diabetic subjects showed an increased plantar pressure in the fore foot region and the heel region. The Diabetic neuropathy group presented with an imbalance in the pressure distribution between the fore foot region and the heel region even without any foot deformity which is a predictive factor for plantar pressure ulcers development. The step length, cadence and walking speed was reduced, and increase step width was observed in both diabetic and diabetic neuropathy subjects without any foot deformities than the control group. These observations from the dynamic plantar pressure measurements will help to design therapeutic footwear for persons with diabetes with total contact soles with specifically designed toe and heel wedges to enhance pressure dissipation and increase comfort.

1. INTRODUCTION

The objective of the study was to evaluate the dynamic foot profile of persons with diabetes using plantar pressure values of the diabetic and diabetic neuropathy subjects during bare foot walking using P-walk plantar pressure analysis system. Subsequent use of the data in improving the design of the therapeutic footwear will be helpful for the diabetic patients in future. There are no substantial tools available for the health care providers as when to prescribe orthotic or therapeutic footwear as a prophylactic measure of ulcer prevention in diabetic neuropathy patients especially during the early stages of neuropathy. Diabetic foot ulcer is the precursor to approximately 85% of the lower extremity amputation in diabetic patients (Margolis 2005).The diabetic foot ulcer is a multi-factorial process with higher chances of ulceration with diabetic neuropathy; Caselli etal (2002) measured plantar pressure in 30 patients with diabetes who had varying degree of diabetic peripheral neuropathy they found that all the patients had an increase in plantar pressure in both the forefoot and hind foot. Early detection of uneven distribution of plantar pressure in the diabetic neuropathy patients has great clinical significance in ulcer prevention. The diabetic committee of American orthopedic foot and ankle society recommends yearly foot examinations in patients with diabetes and more frequent examinations in high risk patients (Pinzur 2005).

This study was aimed to investigate the dynamic planar pressure profiles of persons with diabetes and diabetic neuropathy without any morphological changes or deformities and compare with the control group to design therapeutic footwear to enhance plantar pressure dissipation and increase comfort.

2. MATERIALS & METHODOLOGY

Total of 53 subjects 14 control group subjects (mean age 37.71±8.08 years), 15 type 2 Diabetes mellitus subjects (mean age 47.80±7.58 years) and 24 type 2 Diabetic Neuropathy subjects without any foot deformities (mean age 52.29±7.39 years) took part in the study. D.N subjects who were recruited required to have three areas on the foot where they did not feel a 10 g Monofilament Uzhe etal (2009) and Biothesiometer value of more than 25mv at the great toes i.e. hallux (Jayaprakash etal.2011). Diabetic and diabetic neuropathy subjects were recruited from Prof M.Viswanathan Diabetes research center, Chennai. The hospital ethical committee granted the ethical approval for the present study and all the subjects participating in the study were informed about the study procedure and information consent was obtained from the participant's .The control group subjects were recruited from staff members of CSIR-CLRI.

Before data collection, the subjects were instructed to walk freely in the laboratory to reproduce their typical gait and to feel comfortable at the laboratory. Later the subjects were made to walk on 2 m length BTS-P WALK instrument; the instrument was calibrated for each subject with their respective weight before acquiring the data. The subjects were made to stand still barefoot on the pressure mat and the static pressure during normal relaxed stance was recorded and then subjects were made to walk barefoot over the mat on their own comfortable phase and the dynamic plantar pressure was recorded. Several walking trails were made to familiarize the subject with the system before recording the data to ensure the recording of their normal gait pattern of the subject is obtained.

Table 1a:Peak plantar pressure during dynamic walking

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
Max Pressure (Kpa)	C	14	157.81	17.85	4.77	147.50	168.12	135.60	189.90
	D	15	173.16	17.21	4.44	163.63	182.69	144.60	216.80
	DN	24	174.89	18.51	3.78	167.07	182.70	147.90	228.55

Table 1b: Segmental peak plantar pressure at the M1 and the MH level

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
M 1	C	14	136.46	15.74	4.21	127.37	145.56	107.50	160.50
	D	15	146.30	11.96	3.09	139.68	152.92	127.50	164.00
	D.N	24	144.08	18.71	3.82	136.18	151.98	115.50	197.00
M H	C	14	133.71	20.24	5.41	122.03	145.40	107.50	184.00
	D	15	150.37	19.08	4.93	139.80	160.93	124.00	184.50
	D.N	24	152.06	16.31	3.33	145.17	158.95	110.00	182.00

*M1 – First metatarsal head *MH- Medial heel

Table 2a: ANOVA

		Sum of Squares	Df	Mean Square	F	Sig.
Max Pressure (Kpa)	Between Groups	2802.521	2	1401.261	4.332	.018
	Within Groups	16171.998	50	323.440		

Table 2b: ANOVA

ANOVA						
		Sum of Squares	df	Mean Square	F	Sig.
M 1	Between Groups	784.70	2	392.35	1.477	.238
	Within Groups	13279.47	50	265.59		
M H	Between Groups	3252.56	2	1626.28	4.915	.011
	Within Groups	16545.25	50	330.90		

3. RESULTS & DISCUSSION

The test results descriptive of peak plantar pressure during dynamic walking are shown in **Table 1a** in which the diabetic neuropathy group represented the maximum peak plantar pressure among the three groups. The segmental peak plantar pressure at the M1(metatarsal head) and MH(medial heel) levels are shown in **Table 1b**, which shows the absence of homogenous pressure distribution among the Diabetic neuropathy subjects without any foot deformity. A one-way between groups analysis of variance (ANOVA) was conducted to explore the Dynamic peak plantar pressure at the Metatarsal head (M1) and the Medial heel region (MH) among the control (C), Diabetic (D) and the Diabetic Neuropathy (DN) group scores, and the results are shown in **Table 2a** and **2b**. There was a statistically significant difference ($p<0.05$) in the dynamic peak plantar pressure score for the three groups $F=4.33$.Despite reaching the statistical significance the actual difference in mean scores between groups was quite small. The results shown in the **Table 2b**, relates that there are no significant differences in the segmental Plantar pressure at the M1 (metatarsal heads) between the three groups ($p=0.23$) and an increased medial heel pressure at the MH level in both the diabetic and the diabetic neuropathy group ($p<0.01$) compared to the control group which is contradictory to the earlier studies conducted on the segmental plantar pressure.

Very few studies have been under taken to study the plantar pressure of the diabetic neuropathy patients without any foot deformities. This study has shown a significant increase in the plantar pressure among the diabetic and even in the diabetic neuropathy subjects without any foot deformity in comparison to the control group. An uneven distribution of the plantar pressure in the diabetic neuropathy subjects between MH (Medial heel) and M1 (1st metatarsal head) of the foot was also observed, thus it is evident that the ability to dissipate the plantar pressure is compromised in the diabetic neuropathy subjects even without any foot deformity.

The commercially available diabetic footwear is not suitable for all categories of diabetic neuropathy population. The therapeutic footwear for the diabetic neuropathy patients is custom made for more precise fitting and to ensure a better offloading. The custom made diabetic foot wear is currently developed from the foot mold (plaster of Paris) taken from the patient's directly during a static stance with partial weight bearing, which will not reveal the exact foot dimensions of a dynamic foot while walking. Therefore this data is very valuable and can be utilized to form the last based on the dynamic plantar pressure, and therapeutic footwear to be developed over this last for the diabetic neuropathy foot which is biomechanically efficient way to offload the diabetic neuropathy foot and prevent future foot ulceration.

4. CONCLUSION

Diabetic neuropathy subjects without any acute orthopedic problems and any morphological foot deformities exhibit increase in the peak plantar pressure almost similar to the diabetic subjects, and the segmental pressure analysis showed an increased medial heel pressure levels in both the diabetic and diabetic neuropathy group and there was no significance correlation between the three groups at the M1 1st metatarsal head, proving that there is an inability in homogenous pressure distribution among the diabetic neuropathy subjects even without any deformities and morphological changes of the foot. And gait variation plays an important role in increasing the peak plantar pressure. And the therapeutic foot wear should incorporate features to minimize the foot deformation apart from evenly distributing the plantar pressure.

5. ACKNOWLEDGEMENTS

The authors would like to acknowledge for the project funds from STRAIT 12th five year plan of CSIR CLRI. Authors also extend their sincere thanks to the volunteers from M.V.Hospital for Diabetes and CSIR-CLRI, Chennai for participating in this study.

6. REFERENCES

1. Caselli A, Pham H, Giurini JM, etal, the forefoot to rear foot plantar pressure ratio is increased in sever diabetic neuropathy and can predict foot ulceration, diabetes care, 2002; **25**:1066-1071.
2. Jayaprakash.P, Anil Bhansali, Shobhit Bhansali, Pinaki Dutta, R. Anantharaman, G. Shanmugasundar& M. Ravikiran, Validation of bedside methods measurements evaluation of diabetic peripheral neuropathy, Indian J Med Res,2011 **133**: 645-649.
3. Margolis DJ, Allen-Taylor, Hoffstada, etal, diabetic neuropathic foot ulcers and amputation, Wound Repair Regen, 2005; **13**:230-236.
4. Pinzur MS, Solvenlai MP, Trepman E, Etal, Guidelines for diabetic foot care: recommendations endorsed by the Diabetes Committee of the American Orthopeadic Foot and Ankle Society, Foot Ankle Int,2005;**26(1)**:113-9.
5. uzhe Feng, Felix J. Schlösser, andBauer E. Sumpio,The Semmes Weinstein monofilament examination as a screening tool for diabetic peripheral neuropathy,Journal of vascular surgery 2009;**50**:675-82.

DIP O-37

REDUCTION OF SKIN DISORDERS BY HCHO IN LEATHER PRODUCTS

Daisuke Murai

Consumer Product End-use Research Institute Co., Ltd.
Edobori 2-1-1-20F, Nishi-ku, Osaka, 550-0002, JAPAN
Email:csyh499@dnt.daimaru.co.jp

At JALT (Japan Association of Leather Technology), we are trying to reduce skin disorders caused by leather products containing HCHO. Based on the experience of Japanese tanners, we are now paying closer attention to the effects of using natural and synthetic tanning agents in re-tanning processes.

At the time of manufacturing, many leather products have already been checked by makers for low levels of HCHO. In our previous report, we confirmed the general effects of natural or synthetic tanning agents on keeping HCHO levels low.

The subject of this report is on the possibilities of the long-term effects of these tanning agents on HCHO. In summary, regarding natural and synthetic tanning agents which were added to leather samples in the re-tanning process, HCHO content was measured at the beginning and end of major weathering tests. Also, we have done research on which combinations of tanning agents are suitable for keeping HCHO at low levels at every lifecycle stage. Our goal is to show the effectiveness of these tanning agents in keeping HCHO levels low at all times. Tanning agents are susceptible to color change, for example, when exposed to sunlight, so we are apprehensive of the reduced effectiveness of some tanning agents in reducing HCHO levels. We think it is important that not only leather tanning agents, but materials used at all stages of product manufacturing should be controlled to keep HCHO levels low at all times, from the time of manufacturing to consumption and use, until a product is finally disposed of.

On the other hand, we have another approach to this problem. Because we are the group company of a major Japanese department store, we have exclusive access to our customer's opinions from department store databases. Our database registers more than 400 opinions about leather products every year including various opinions about discoloration, sub-standard craftsmanship, and so on, totaling over 10,000 opinions from 1996. We must utilize this information to improve product quality and revenue. We will show that the survey of our database indicates the tendency of reducing the incidence of skin disorders as time passes from first-time consumer use.

Keywords: HCHO skin disorder natural tanning agent

1. INTRODUCTION

In this report, we study about whether or not the effect of HCHO reduction by natural or synthetic tannins is kept for long time. Although tannins are generally said to be weak to sunlight, the urability of the effect is tested for find a correlation with leather discoloration. Also, we study the influence from external migration.

2. MATERIAL AND METHODS

2.1 Materials

2.1.1 Natural tannin leather

The bovine Wet-blue (WB) were re-tanned by synthetic tannin at 4% of WB weight, and natural tannin was further added at 5% of WB weight, respectively.

2.1.2 Synthetic tannin leather

The bovine Wet-blue (WB) were re-tanned by synthetic tannin agent and fat-liquored. The amount of synthetic tannin agent used was 4% of WB weight, respectively.

2.2 Tannin agents used

2.2.1 Natural tannin

The 4 types (Mimosa, Chestnut, Quebracho, Tara) were selected as typical re-tannin agents distributed in the market. And it was combined the 3 types (A, F, G) of synthetic tannin agents.

Table 1 The natural tanning agent added

Natural tannin agent	
ME	Mimosa
CH	Chestnut
KE	Quebracho
TA	Tara

Table 2 The synthetic re-tanning agent used

Synthetic tannin agent	Main component
A	Dicyandiamide
F	Phenol condensate
G	Melamine-based condensation mixture

2.2.2 Synthetic tannin

The 3 types (A, F, G) were selected as typical re-tanning agents distributed in the market. It was used the same as above.

2.3 Test Method

2.3.1 Migration of HCHO

The surfaces of formaldehyde tanned (C0) leather and sample leather were overlapped and sealed in a polyethylene bag, leaved for 24 hours. (Leather C0: HCHO content is 200 mg/kg)

2.3.2 Durability test (Weathering test)

Based on JIS L 0843 Test methods for colour fastness to xenon arc lamp light (ISO 105-B02). Exposure method was #3 and exposure time was grade 4 (The standard Blue-scale No.4 change color to grade 4 on grayscale).

2.3.3 Measuring HCHO content

The formaldehyde content is measured by acetyl-acetone method, ISO 17226-2:2008. (In this study, but not exactly, we measure to HCHO content less than 16 mg/kg, as a reference. In general, less than 16 mg/kg is recorded “Not Detected”.)

3. Analysis of consumer’s complaints

We have exclusive access to our customer's opinions from Japanese major department store databases. The database has more than 10,000 opinions and test report on leather items from 1996. The examples of skin disorder were extracted from the database. And it compare with the tendency of all leather products as a whole.

4. Result and Discussion

4.1 Durability of HCHO reduction effect

Durability of formaldehyde reduction effect by natural tannin and synthetic tannin was investigated. In general, tannins have properties such as discoloration due to sunlight, so this report examined the presence or absence of aged deterioration due to sunlight.

From table 3, there was almost no effect of sunlight on the content of HCHO in leather containing natural tannin. On the other hand, a color change was seen in some leather. From these result, it seem that there is no correlation between discoloration by aging and the effect of HCHO reduction by tannin. It shows that, there is a durability of HCHO reduction effect by natural tanning.

Table 3 Change of HCHO content (mg/kg) before and after weathering test

Natural	Synthetics	Initial	Weathered	CH(Color change)
ME	A	34	30 (-4)	3
ME	F	-	20	2.5
ME	G	-	16	3
CH	A	44	35 (-9)	4.5
CH	F	-	26	4
CH	G	37	-	-
KE	A	34	32 (-2)	4
KE	F	19	22 (+3)	2.5
KE	G	-	19	1.5
TA	A	41	38 (-3)	3.5
TA	F	-	-	-
TA	G	-	18	4

Subsequently, also on synthetic tannin agents, even though it had exposed sunlight, it showed that no increase in HCHO content was observed (Table 4). That is, the effect of HCHO reduction was kept in. However, unlike natural tannins, leather discoloration was not seen much.

Table 4 Change of HCHO content (mg/kg) before and after weathering test

Synthetic	Content	Initial	Weathered	CH(Color change)
A	2%	48	44 (-4)	3.5
A	4%	112	104 (-8)	4
A	6%	181	163 (-18)	3.5
F	2%	269	191 (-78)	4
F	4%	319	228 (-91)	4
F	6%	467	343 (-124)	4
G	2%	81	38 (-43)	4
G	4%	166	76 (-90)	4
G	6%	321	173 (-148)	4

4.2 Durability of HCHO migration effect

In order to confirm the effect of HCHO reduction by tannins, after the above durability test, it was also tested that the influence of external migration. Compare with “Migrated only”, the HCHO content tended to increase slightly in “Weathered + Migrated”. That is, the performance down by aged was slight, and it was not confirmed big performance down.

Table 5 Change of HCHO content (mg/kg) before and after migration test

Natural	Synthetics	Initial	Migrated only	Weathered + Migrated
ME	A	34	42 (+8)	50 (+16)
ME	F	-	20	38
ME	G	-	16	36
CH	A	44	46 (+2)	57 (+13)
CH	F	-	26	45
CH	G	37	-	-
KE	A	34	-	56 (+22)
KE	F	19	22 (+3)	43 (+24)
KE	G	-	19	39
TA	A	41	-	52 (+11)
TA	F	-	-	-
TA	G	-	18	37

Also on synthetic tannin, compare with "Migrated only", the HCHO content is little increasing in "Weathered + Migrated". It seem that the influence of external migration is little increased by aged. The performance of HCHO reduction is little downed.

Table 6 Change of HCHO content (mg/kg) before and after migration test

Synthetics	Content	Initial	Migrated Only	Weathered + Migrated
A	2%	48	55 (+7)	52 (+4)
A	4%	112	121 (+9)	111 (-1)
A	6%	181	196 (+15)	165 (-16)
F	2%	269	253 (-16)	203 (-66)
F	4%	319	296 (-23)	236 (-83)
F	6%	467	420 (-47)	342 (-125)
G	2%	81	86 (+5)	50 (-31)
G	4%	166	157 (-9)	88 (-78)
G	6%	321	299 (-22)	166 (-155)

4.2 Customer's complaint

Unlike the previous experiments, we show the actual complaint on leather products in Japanese department stores. Firstly, on women's shoes, there is two major complaint. One is color bleeding and fading. The other is irregularity break. It is more than half by the two major complaints. On the other hand, the number of complaints on skin disorders are not large.

Table 7 Major quality complaint of women's shoe in 2013 to 2015

Item	Number of complaint
Color bleeding and fading and scratch	135 (20%)
Irregularity break, premature wear, ripping at seam	268 (41%)
Rough finish, slipping, shoe sore	111 (17%)
Performance, feeling of use	119 (18%)
Other	28 (4%)

The same tendency is shown for women's bags, too. There is two major complaint. One is color bleeding and fading. The other is irregularity break. It is more than half by two major complaints, and the number of complaints on skin disorders are not large, too.

Recently, it is often used that thin and light leather for fashion items, so it is often seen that ripping at seam. Compared the before ago, leather products are not only long-life, but our customers do not think so. While light leather products are often sold, but complaints of strength are endless.

Table 8 Major quality complaint of women's bag in 2013 to 2015

Item	Number of complaint
Color bleeding and fading and scratch	172 (37%)
Irregularity break, premature wear, ripping at seam	172 (37%
Rough finish	37 (8%)
Performance, feeling of use	31 (7%)
Other	49 (11%)

Returning to the main subject here, we show that the tendency of complaint on skin damaged. It is small number from the whole, skin disorders caused by leather products is as follows (Table 9). Many cases were unclear, it is not only due to HCHO.

Table 9 Number of complaint in 2008 to 2013

Items	Skin damaged	Total
Jackets (textiles)	13	1045
Leather wear	0	109
Leather shoes	7	1836
Leather bags	3	1031
Leather watch bands	3	88

Although complaints on skin disorder are few, it is clear that the trend of occurrence timing (Table 10). The examples are concentrated early use. Over time, the occurrence of skin disorders is clearly decreasing. The trend is also equal with our sense of life. It show that there is no problem with old familiar leather goods. It should be careful after purchase immediately.

Table 10 Number of complained timings in 2008 to 2013

Wearing period	Skin damaged
First time	6
Within one month	11
Within six months	6
Within one year	0
Over one year	3
Unknown	0

4.3 CONCLUSION

The effect of HCHO reduction by tannin is kept not only at the time of manufacturing and sales, but also consuming stage. We are hope for safety in manufacturing, and sales, usage, until waste, there is a possibility that tannins will be useful for reduction of skin disorders by HCHO in leather.

Currently, leather industry is making effort to reduce HCHO at manufacture. Is this correct? The answer is in use stage in product-life. And then, by our survey, skin disorders are often occurred in new condition. It seems to be correct, now.

5. Acknowledgements

We gratefully acknowledge the work of past and present members of our company, and Japan Association of Leather Technology (JALT), The DAIMARU-MATSUZAKAYA department stores.

6. References

1. JALT: Development and Practical Application Report for Japanese eco-leather (2008-2015)

DIP O-38

COMPARISION OF VISUAL ASORTING PROCESS AND SPECTRAL PHOTOMETER USAGE IN LEATHER APPAREL PRODUCTION

Mehmet Mete MUTLU*, Nilay ORK, Altug IMECE, Pelin GORKEM

Ege University, Engineering Faculty, Department of Leather Engineering, Bornova, Izmir, 35100, Turkey
Email:mete.mutlu@ege.edu.tr

Leather apparel production consists of many steps following each other systematically. Each process step has its own importance and effect on quality. The properties of the material are important as well as design, pattern, well fitting, sewing and handiwork on the garment. Since each leather has its individual properties, leathers are assorted to constitute small homogeneous groups under standard light conditions considering their colours, handle, touch and surface appearance. Thus, assorting process plays an important role on quality of a leather garment. This process is carried out by assorting experts in a company depending on their experience and organoleptic controls. The aim of this study is to compare visual colour assessments of experts with the data obtained from a spectral photometer by using different CIE colour difference formulas and to determine the best formula matching to human assessments. The study was conducted in a leather apparel production company with 3 different colours (dark brown, whiskey brown and maroon) and 115 nappa goat leathers were used. Similar leathers were grouped as 5 or 6 to be manufactured as one leather jacket in assorting process by the experts. Then the colour differences of leathers in a group were measured by a spectrophotometer and evaluated with CIE76, CIE2000 and CIE94 colour difference formulas. Colour of each leather was measured from 7 different regions and the data were compared with the visual assessments statistically. As a conclusion CIE2000 colour formula matched best with the results of the human experts with 73% success.

Keywords: Leather Apparel, Assort, Spectral Photometer, Colour Measurement

INTRODUCTION

Leather is a sheet material with the area of each piece ranging from tens of square centimetres to six, seven or more square meters depending on the animal from which it was obtained. Until the development of woven textiles it was the only material available in sheets of this size (Thomson R. and Kite M., 2006). Producing garments from leathers have significant differences than textiles because leather is not a uniform material from dimensional and structural perspectives. The physical properties of leather change depending on the animal type and the animal individually. Furthermore these properties exhibit variations in different parts over the leather area (Mutlu M M, et. al, 2014). Thus, leather garments are made up of many small patterns.

The leather apparel manufacturing begins with assortment process which is separation and selection the finished leathers by objective method accordingly the area to be used. In this processes finished leathers are separated into small groups showing similar texture, colour, quality and feel properties which finally provides uniform production. The properties of leathers constituting a leather garment should be similar for standard production (Dogan A and Asil N, 1996).

Quality and colour are two important factors in assort process. Firstly, leathers are inspected from a quality aspect of view. In quality assorting thickness, grain uniformity, shape and area properties are also considered. Low quality leathers which cannot even be used in non-seen inner parts are rejected. Second important inspection is the colour assorting. Leathers with the same tones are collected in a certain number of groups. For example, for a standard leather jacket approximately five to seven sheep leathers are grouped together in assorting depending on the model and leather sizes (Fig 1). The performance of the assorting process highly depends on the experience and practice of the expert in the charge of assorting.
The assorting expert should:

- know the leather material well
- know the model to be produced
- plan the usage of leathers with defected areas

The assorting expert should consider the work of the cutter who takes the grouped leathers, opens the piles, places the patterns on the leathers and does the cutting with snap blade knives or special knives. The cutter should:

- work with minimum error
- do the cutting with minimum waste for the model
- work quick and fast
- use good areas of leathers with patterns at most seen parts and reserve weak or minor defected areas for unseen parts

Right and good illumination is necessary for assorting and also cutting processes. The tables used in assorting process should not have reflective surface. The tables used in cutting process should be covered with 90x90 or 100x100cm glass and have approximately 15 degree of slope.

Fig.1. Assorting process in leather garment manufacture

Colour has a big importance in the modern world, because in most cases, colour is an important factor to be adjusted in production of a product and has vital importance on the commercial success of the consumer goods. In other words, colour is a decision factor on quality, attraction and sales of a product. Colour is combination of physical, physiological and psychological perceptions in our visual system caused by the light reflected from an object.

Poor colour memory, eye fatigue, colour blindness and viewing conditions can all affect the human eye's ability to distinguish colour differences. In addition to those limitations, the eye does not detect differences in hue (red, yellow, green, blue, etc.), chroma (saturation) or lightness equally. In fact, the average observer will see hue differences first, chroma differences second and lightness differences last (X-rite incorporated, 2007). Instrumental method is a precise way of colour measurement. Spectrophotometers measure the reflections of light at certain wavelengths for example from 400 to 700nms reflecting from the object and convert the data into various colour systems developed based on human visual system.

Even though a tolerance limit for colour difference is determined according to colour systems, the tolerances are not always be compatible with real world results. The aim of this study was to monitor the work of a assorting expert in a leather manufacturing company, to examine his/her results by using different colour difference evaluation formulas, to compare the results statistically and to determine the formulas which are in accordance with the real world experiences. Thus, instrumental colour measurement can be used in assorting process to minimize colour errors.

MATERIAL AND METHODS

Material

Totally 115 nappa goat leathers which have 3 different colours (dark brown, whiskey brown and maroon) were used as material.

Minolta CM-508d portable spectrophotometer having 8mm measurement area were used for surface colour measurements. The measurement data were collected by using SpectraMagic NX Software. The data were evaluated by using SPSS statistics software.

Methods

Similar leathers were grouped as five or six to be manufactured as one leather jacket in assorting process by the experts in a leather garment producing company. A total number of 115 leathers were selected for production. Colour measurements were done from 7 different areas for each leather (Fig 2). Colour differences of leathers were determined using CIE76, CIE94 and CIE2000 colour difference formulas. The conformity of assorting expert's selection and the colour difference evaluation formulas were tested by using Wilcoxon signed-rank test which is a non-parametric statistical hypothesis test (Senol S, 2004).

Fig.2. Colour measurement locations on leather and measuring 3 different coloured leathers

Colour Difference Formulas

A color difference formula or a color difference metric, which measures the difference between two colors, is becoming a prime research topic in the modern colorimetry. The target is to find a good color difference formula, which can give a quantitative measure (ΔE) of the perceived color difference correctly. It is also the requirement of many color applied fields such as image analysis, color reproduction, color image restoration and so on (Pant D R, Farup I, 2012).

History of CIE Colour-Difference formulas can be summized as (Melgosa M, 2013)

1964: CIE 1964 (U*V*W*)

1976: CIE 1976 (L*u*v*) = CIELUV

1976: CIE 1976 (L*a*b*) = CIELAB

1995: CIE94

2000: CIEDE2000

CIE76 Colour Difference System

In 1976 the CIE published the first internationally endorsed color differencing equation. This formula called ΔEab or ΔE76 has been used in many ISO procedures. The color notation used for this equation was the L*a*b*-color space (Habekost M, 2016). In CIELab Colour System, L* defines lightness, a* denotes the red/green value and b* the yellow/blue value. Colour differences are directly calculated from the difference of coordinates values of sample and standard. When tolerancing with CIELAB, you must choose a difference limit for ΔL* (lightness), Δa* (red/green), and Δb* (yellow/blue). These limits create a rectangular tolerance box (Fig 3) around the standard. The linear distance between sample and standard is calculated and expressed as ΔE. (X-rite incorporated, 2007).

$\Delta L = L_{sample} - L_{standard}$ ΔL = + lighter , - darker

$\Delta a = a_{sample} - a_{standard}$ Δa = + redder , - greener

$\Delta b = b_{sample} - b_{standard}$ Δb = + yellower , - bluer

$$\Delta E^*_{ab} = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

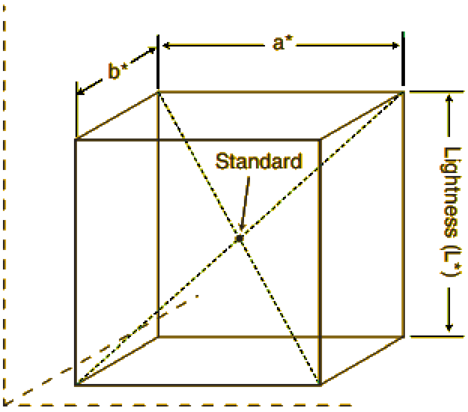


Figure 3. CIELAB Tolerance Box

CIE94 Colour Difference System

The CIE94 calculation uses CIE LCh colour space. The L*C*h color space, similar to CIELAB, is preferred by some industry professionals because its system correlates well with how the human eye perceives color. It has the same diagram as the L*a*b* color space but uses cylindrical coordinates instead of rectangular coordinates. In this color space, L* indicates lightness, C* represents chroma, and h is the hue angle. The value of chroma C* is the distance from the lightness axis (L*) and starts at 0 in the center. Hue angle starts at the +a* axis and is expressed in degrees (e.g., 0° is +a*, or red, and 90° is +b, or yellow) (Konica Minolta, 2015).

The CIE94 calculation mathematically defines an ellipsoid around the standard colour with semi-axis corresponding to hue, chroma and lightness. The ellipsoid represents the volume of acceptable colour and automatically varies in size and shape depending on the position of the colour in colour space. The user can change lightness (kL) to chroma (Kc) ratio. These settings affect the size and shape of the ellipsoid in a manner similar to how the l:c and cf settings affect CMC. (X-rite incorporated, 2007).

$$\Delta E_{94}^* = \sqrt{\left(\frac{\Delta L^*}{k_L S_L}\right)^2 + \left(\frac{\Delta C_{ab}^*}{k_C S_C}\right)^2 + \left(\frac{\Delta H_{ab}^*}{k_H S_H}\right)^2}$$

$$\begin{aligned}
&\Delta L^* = L_1^* - L_2^* \\
&C_1^* = \sqrt{{a_1^*}^2 + {b_1^*}^2} \\
&C_2^* = \sqrt{{a_2^*}^2 + {b_2^*}^2} \\
&\Delta C_{ab}^* = C_1^* - C_2^* \\
&\Delta H_{ab}^* = \sqrt{{\Delta E_{ab}^*}^2 - {\Delta L^*}^2 - {\Delta C_{ab}^*}^2} = \sqrt{{\Delta a^*}^2 + {\Delta b^*}^2 - {\Delta C_{ab}^*}^2} \\
&\Delta a^* = a_1^* - a_2^* \\
&\Delta b^* = b_1^* - b_2^* \\
&S_L = 1 \\
&S_C = 1 + K_1 C_1^* \\
&S_H = 1 + K_2 C_1^*
\end{aligned}$$

CIE2000 Colour Difference Formula

CIE is totally a new formula obtained from enhancement of CIE Lab 94 formula and published as Improvement to industrial colour-difference evaluation (CIE 2001). In this formula first a partial correction is done on red-green axis and evaluation is done in the new formed colour space (X-rite incorporated, 2007).

$$\Delta E_{00}^* = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \frac{\Delta C'}{k_C S_C} \frac{\Delta H'}{k_H S_H}}$$

$$\begin{aligned}
&\Delta L' = L_2^* - L_1^* \\
&\bar{L} = \frac{L_1^* + L_2^*}{2} \quad \bar{C} = \frac{C_1^* + C_2^*}{2} \\
&a_1' = a_1^* + \frac{a_1^*}{2}\left(1 - \sqrt{\frac{\bar{C}^7}{\bar{C}^7 + 25^7}}\right) \quad a_2' = a_2^* + \frac{a_2^*}{2}\left(1 - \sqrt{\frac{\bar{C}^7}{\bar{C}^7 + 25^7}}\right) \\
&\bar{C}' = \frac{C_1' + C_2'}{2} \text{ and } \Delta C' = C_2' - C_1' \quad \text{where } C_1' = \sqrt{a_1'^2 + b_1^{*2}} \quad C_2' = \sqrt{a_2'^2 + b_2^{*2}} \\
&h_1' = \operatorname{atan2}(b_1^*, a_1') \mod 360^\circ, \quad h_2' = \operatorname{atan2}(b_2^*, a_2') \mod 360^\circ
\end{aligned}$$

$$\Delta h' = \begin{cases} h_2' - h_1' & |h_1' - h_2'| \leq 180^\circ \\ h_2' - h_1' + 360^\circ & |h_1' - h_2'| > 180^\circ, h_2' \leq h_1' \\ h_2' - h_1' - 360^\circ & |h_1' - h_2'| > 180^\circ, h_2' > h_1' \end{cases}$$

$$\Delta H' = 2\sqrt{C_1' C_2'} \sin(\Delta h'/2), \quad \bar{H}' = \begin{cases} (h_1' + h_2' + 360^\circ)/2 & |h_1' - h_2'| > 180^\circ \\ (h_1' + h_2')/2 & |h_1' - h_2'| \leq 180^\circ \end{cases}$$

$$T = 1 - 0.17\cos(\bar{H}' - 30^\circ) + 0.24\cos(2\bar{H}') + 0.32\cos(3\bar{H}' + 6^\circ) - 0.20\cos(4\bar{H}' - 63^\circ)$$

$$S_L = 1 + \frac{0.015\left(\bar{L} - 50\right)^2}{\sqrt{20 + \left(\bar{L} - 50\right)^2}} \quad S_C = 1 + 0.045\bar{C}' \quad S_H = 1 + 0.015\bar{C}'T$$

$$R_T = -2\sqrt{\frac{\bar{C}'^7}{\bar{C}'^7 + 25^7}} \sin\left[60^\circ \cdot \exp\left(-\left[\frac{\bar{H}' - 275^\circ}{25^\circ}\right]^2\right)\right]$$

RESULTS AND DISCUSSION

Hypothesis for Wilcoxon signed-rank test for 0.5 and 1.0 tolerance limits for CIE 76, CIE 2000 and CIE 94 colour difference formulas were as following:

$H_0: \mu > 0.5$ $H_0: \mu > 1.0$

$H_1: \mu \leq 0.5$ $H_1: \mu \leq 1.0$

The rejection of $H_0: \mu > 0.5$ and $H_0: \mu > 1.0$ hypothesis and acceptance of $H_1: \mu \leq 0.5$ and $H_1: \mu \leq 1.0$ hypothesis confirm that there is an accordance between the choice of machine and choice of the assorting expert by visual system.

Table.1. Acceptance or rejection status of Ho>0.5 and Ho>0.1 hypothesis for CIE76, CIE2000 and CIE94 colour difference formulas

	Ho: μ >0.5 Hypothesis				Ho: μ >1.0 Hypothesis		
	CIE76	CIE2000	CIE 94		CIE76	CIE2000	CIE 94
D. brown s1	REJECT	REJECT	Accept		REJECT	REJECT	Accept
D. brown s2	REJECT	REJECT	Accept		REJECT	REJECT	Accept
D. brown s3	REJECT	REJECT	Accept		REJECT	REJECT	REJECT
D. brown s4	REJECT	REJECT	Accept		REJECT	REJECT	Accept
D. brown s5	REJECT	REJECT	Accept		REJECT	REJECT	Accept
D. brown s6	REJECT	REJECT	Accept		REJECT	REJECT	REJECT
D. brown s7	REJECT	REJECT	Accept		REJECT	REJECT	Accept
D. brown s8	REJECT	REJECT	Accept		REJECT	REJECT	Accept
D. brown s9	REJECT	REJECT	Accept		REJECT	REJECT	Accept
D. brown s10	REJECT	REJECT	Accept		REJECT	REJECT	Accept
w. brown s1	Accept	Accept	Accept		REJECT	REJECT	REJECT
w. brown s2	Accept	Accept	Accept		Accept	Accept	Accept
w. brown s3	Accept	Accept	Accept		Accept	Accept	Accept
w. brown s4	Accept	Accept	Accept		Accept	Accept	Accept
w. brown s5	Accept	Accept	Accept		Accept	Accept	Accept
w. brown s6	Accept	Accept	Accept		Accept	Accept	Accept
w. brown s7	Accept	Accept	Accept		Accept	Accept	Accept
Maroon s1	Accept	Accept	Accept		Accept	REJECT	REJECT
Maroon s2	REJECT	REJECT	REJECT		REJECT	REJECT	REJECT
Maroon s3	Accept	Accept	REJECT		Accept	REJECT	REJECT
Maroon s4	Accept	Accept	REJECT		Accept	REJECT	REJECT
Maroon s5	Accept	Accept	REJECT		REJECT	REJECT	REJECT

In textile 0.5 median figure or in other words tolerance value is used for colour quality control because textile is generally a more homogenous material. However for more un-uniform materials like leather due to its natural character, a higher tolerance limit 1.0 is taken. In figure x and y, pie chart graphics of Ho>0,5 and Ho>1.0 hypothesis for CIE76, CIE2000 and CIE94 colour difference formulas are given.

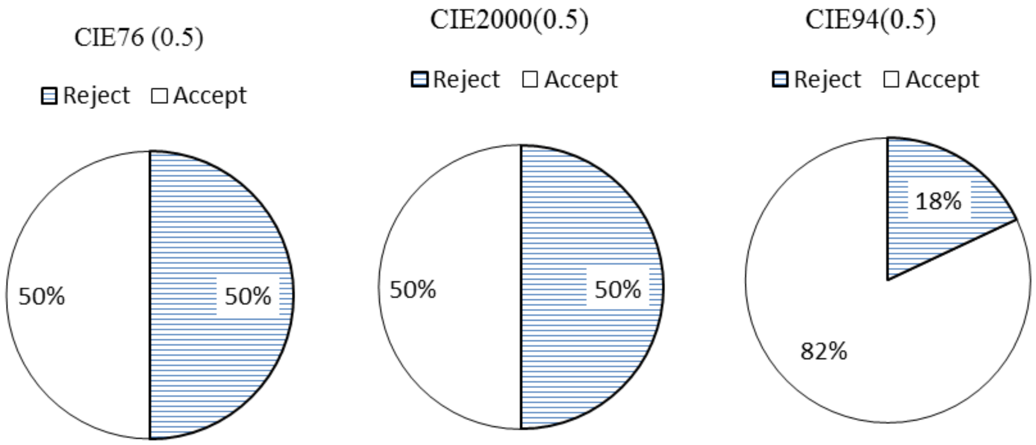


Figure 1. Ho>0.5 hypothesis for CIE76, CIE2000 and CIE94 colour difference formulas

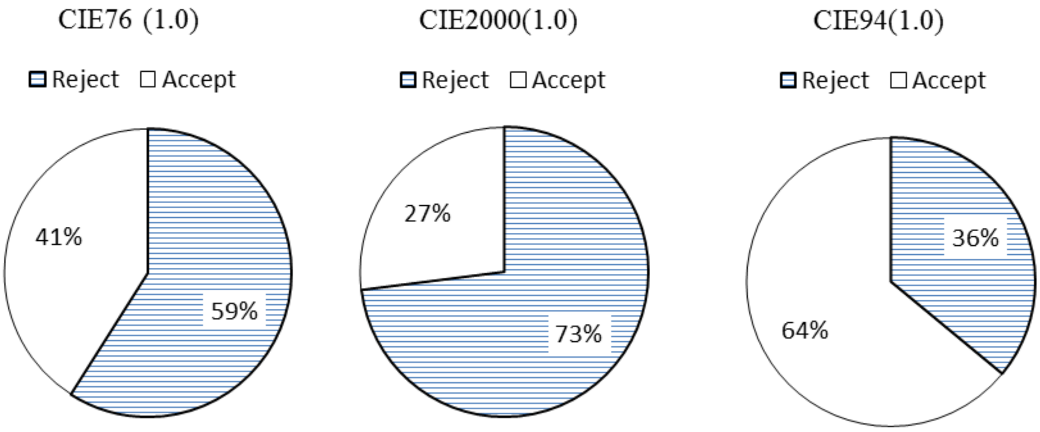


Figure 2. Ho>0.1 hypothesis for CIE76, CIE2000 and CIE94 colour difference formulas

When figure 1 and figure 2 are inspected it can be seen that CIE76 and CIE2000 colour difference formulas show 50% conformity and CIE94 shows only 18% conformity with the visual evaluations at 0.5 tolerance limit. When the tolerance limit is selected 1.0, which is better for an un-uniform material like leather, CIE2000, CIE76 and CIE94 colour difference formulas show 73%, 59% and 36% conformity with the visual evaluations respectively. So the results of equations from best to worst fit follows the order CIEDE2000 > CIE76 > CIE94 for nappa goat leathers used for leather garment production.

Jawahar et.al 2015 have studied the Correlation of visual and instrumental color measurements to establish color tolerance using regression analysis with a commercial batch of dyed suede garment leathers (220 leathers) in grayish black shade and found the results of equations from best to worst fit follows the order CMC(2:1) > CIE94 > CIEDE2000 > CIE76. However, while CMC is targeted for use in the textile industry, CIE94 is targeted for use in the paint and coatings industry. You should consider the type of surface being measured when choosing between these two tolerances. If the surface is textured or irregular, CMC may be the best fit. If the surface is smooth and regular, CIE94 may be the best choice. (X-rite incorporated, 2007).

CONCLUSION

There are various colour difference and tolerance formulas developed to measure the colour difference of two samples, which is important to ensure quality control. The aim of these formulas is to obtain results, confirming human visual perception. However material properties and visual perception are two important factors effecting the succes of a formula. So colour difference formulas is becoming a popular research topic in the modern colorimetry.

In this study it was inspected which colour difference formula was performing similar to selections of assorting expert in a leather garment producing company. From the statistical evaluation of data, it was found that the adaptibility of equations to real life observations from best to worst fit follows the order CIE DE2000 > CIE76 > CIE94 for nappa goat leathers. CIE 2000 colour difference formula with 1.0 tolerance setting showed highest compatibility by 73% success comparing with visual inspection and can be used in practice. Surface properties of the material should be considered when choosing a colour difference equation to use. 1.0 tolerance value for colour difference formulas works better for leather samples than 0.5 tolerance.

ACKNOWLEDGEMENTS

References

1. CIE. Improvement to industrial colour-difference evaluation. Vienna: CIE Publication No. 142-2001, Central Bureau of the CIE; 2001.
2. Dogan A, Asil N. Deri Giyim Sanayisinde Faaliyet Gösteren Üç İşletmede Bir Verimlilik Göstergesi Olarak Kayıp Zamanlar, Milli Prodüktivite Merkezi Yayınları, Ankara, 1996. Yayın No: 582, 59 s.
3. Habekost M, Which color differencing equation should be used?, International Circular of Graphic Education and Research, No. 6, 2013
4. Jawahar M, Kanth S V, Venba R, Babu N K C, Correlation of visual and instrumental color measurements to establish color tolerance using regression analysis, Journal- American Leather Chemists Association 110(12):409-419 · December 2015
5. Konica Minolta, Understanding the CIE L*C*h Color Space, http://sensing.konicaminolta.us/2015/03/understanding-the-cie-lch-color-space/ , 2015. (accessed December 2016)
6. Melgosa M, CIE/ISO new standard: CIEDE2000, Workshop, University of Leeds (UK), 4 July 2013
7. Mutlu M M, Ork N, Yegin O, Bas S, Mapping the Variations of Tensile Strength over the Area of Sheepskin Leather, Annals of the University of Oradea Fascicle of Textiles, Leatherwork, 2014, Vol XV, Nr.1, pp 157-162.
8. Pant D R, Farup I, Rienannian Formulation and comparison of Color Difference Formulas, Proceedings of the 18th Color and Imaging Conference, Texas, USA, 2010
9. R. Thomson and M. Kite, Conservation of leather and related materials, Elsevier Linacre House, Jordan Hill, Oxford, 2006, pp. 1.

10. Senol, S., Parametrik Olmayan İstatistik, Ege Ü. Basımevi, Fen Fak. Yay. No:190 (307 sf.), (ISBN: 975–483–638–8) , Bornova/İzmir. 2004
11. X-rite Incorporated, A Guide to Understanding Color Communication, http://www.xrite.com/learning/whitepapers, 2007 (accessed December 2016)

E-LEARNING AND BLENDED TRAINING IN THE LEATHER PROFESSIONAL EDUCATION

Ivan Kráľ

Email:i.kral@unido.org

Industrial development increasingly requires knowledge that is generated by R&D and experience, and subsequently, passed on to those working in the leather-related subsector. Globalization, rapid changes in market conditions and technology, needs of catering for environmental and social aspects of the manufacturing processes call for higher efficiency and effectiveness of acquiring necessary knowledge at all level of the leather-related business.

Traditional or conventional learning methods include face-to-face (classroom, personal instruction, tutoring, on-the-job) and asynchronous approaches such as self-study and distance learning. These methods are not without challenges. They all lack learner's focus and interactivity, they are geographically and time limited, and results based around averages. Using today's ICT with special references to multimedia applications and networking (in its broadest sense) provides the basis for **e-Learning**by ensuring interactivity and the full involvement of learners. In the e-Learning environment content is organized according to the needs and the profile of the learner, whereas progress and results are recorded, learners have the opportunity to consult (with teachers and with other learner fellows) without moving from their location. The two major components and drivers of e-Learning are the learning content development (LCD) and the learning management systems (LMS) – though the latter is not an inevitable service.

Existing knowledge available in any electronic format may be used for composing e-Learning content. To demonstrate the potential of this new technology UNIDO has developed complete e-Learning courses regarding sustainable leather processing, tannery effluent treatment, footwear pattern engineering and footwear technology that may be used for conventional, as well as individual training. These courses now are available at www.leatherpanel.org.

Key words: eLearning; skills development, training, training in the leather value chain, UNIDO

INTRODUCTION:

Human resources are crucial for the sector's competitiveness, and UNIDO understand the importance of training. For competing in the market on quality, product consistency and performance, fashion and service to customers, skilled personnel are essential. The combination of experience and youth, i.e. skilled workers and young applicants, represents the key asset on which the competitiveness of the sector is based. This can be enhanced at sector level by developing continuing vocational training and life-long learning.

Traditional learning/training practice

Conventional or traditional learning styles are dominated by the rather passive attitude of the learner The well-known forms are as follows:

1. **Face-to-face learning** arrangements are based on the teacher directing and/or managing the learning process. This is still the most widely used method which may be one of the followings:

a. classroom;
b. tuition;
c. workshop, seminar, small group discussion
d. conferences or congresses;
e. similarly meetings (e.g. at work), trade fairs and exhibitions also serve as learning opportunities as they also facilitate knowledge transfer.

2. With **on-the-the job training** (OJT) or **job-embedded learning** or apprenticeship student receive training whilst remaining in the workplace and learn about and participating in the job tasks. This is one of the best ways for a person to learn new skills and gain valuable experience.

3. **Self-study training** is the educational process where individuals learn independently.

4. **Distance learning** (or **distributed learning**) focuses on teaching students who are not physically present in a traditional educational setting such as a classroom

Traditional means teaching tools/ media storing and used for imparting knowledge include:

a) paper (hard copies of textbooks, catalogues, magazines, guidelines, user's manuals etc.);

b) audio-visual tools such as slide, ppt presentations, video projections and recorded voice;

c) samples, models, mock-ups and real (functional) objects used for demonstrating practical aspects of the knowledge to be conveyed.

Primary restrictions of traditional classroom training for the Learner include:

- Inherently places value on standards, curriculum and test results resulting in resulting in limited focus on the big picture of the Learner's progress,
- lacks emphasis on larger concepts or structures as it focuses on basic skills and gradually builds to a whole;
- lacks interactivity: learners receive few opportunities to practice group dynamics and teamwork;
- pulls results around averages as it cannot devote sufficient times and efforts to those advancing slower and/or provide better learners with more and higher level resources to develop their specific capacities;
- timely and geographically limited that requires synchronization of physical presence of all parties concerned;

- provides limited potential for developing competencies that would enable learners further enhancing their abilities.

All of these restrictions in UNIDO's experiences lead to high costs, low efficiency and effectiveness. Moreover, refreshing knowledge base to be imparted – especially in case of using static (document-oriented) media – requires involves additional expenses.

New tools in training

The range of these conventional styles and media are now being substantially expanded by the rapidly developing information and computer technology (ICT). Traditional (learning, text) books are now being replaced by their electronic versions such as documents produced on computers (mostly in PDF format), presentations, videos and e-books. Communication between teachers and learners is now possible by using computerized networks (the world-wide web – WWW and e-mail, skype and others).

Schools, colleges, institutions and organizations – including those inside of manufacturing and trading companies – engaged with education and training adapt ICT in their operations. Beamers and electronic boards are becoming usual equipment in classrooms, electronic network facilities are used more and more in communication among teachers, learners and even parents, teachers use projected presentations in delivering courses and use computers for tests or even examinations.

Learning content and learning content development

The material base and the processing/manufacturing technology has gone a long way in the past years and decades. Related training contents (i.e. the knowledge base and range of skills) have also changed – though by at far slower pace than the technology – but their structures and related training systems seem to be more rigid.

Medium level educational and training institutions imparting knowledge and providing certificates to those successfully completing their courses try to cope with technical development. Quite naturally, they are always somewhat behind in incorporating most advanced and newest (especially technical) development as innovative solutions are coming from suppliers (e.g. materials, equipment/hardware, software) and R&D organizations or developed within the manufacturing environment (e.g. production and management systems, marketing methods).

The other challenge is globalization when the leather-based industry, at least its manufacturing base is disappearing from industrialized countries. Massive production capacities are emerging in countries having no or little tradition in this trade. At the same time utilization of the extensive knowledge base and experience accumulated in professional education and training is not only seriously handicapped, whilst developing similar intellectual support services in new regions would take quite some time.

Online learning/e-Learning

Education in which instruction and content are delivered primarily over the Internet is referred today as online learning or e-Learning.

Practitioners have further defined key terminology associated with e-Learning. The below vocabulary bank is often referred to discussing e-Learning:

- **Blended learning** is any time a student learns at least in part at a supervised brick-and-mortar location away from home and at least in part through online delivery with some element of student control over time, place, path, and/or pace.
- **Computer Assisted Instruction (CAI**) is the use of educational software to enhance the mastering of educational concepts or standards without the involvement of a teacher.
- The **content repository** is a venue for saving and sharing content. A digital content repository is an online venue for saving and sharing digital content.
- **e-School**: a formally constituted organization that offers fulltime education delivered primarily over the Internet.
- **Home-grown content** is developed by a teacher, school, or district for use in instruction, as compared to content developed by outside companies or other vendors.
- The **instructional media** is the materials that teachers use to teach and students use to learn (for example, printed text, digitized text, software, speech, images).
- The **online facilitator** is used in two ways:

(i) For part-time online programs is the person working face-to-face with the online student to monitor student progress and attendance, providing training, assist in motivating the student, etc. The person may or may not be a certified teacher but works in conjunction with the certified online teacher.

(ii) Used interchangeably with online teacher or online educator.

- **Video conferencing** is interactive communication technologies which allow two or more locations to interact via two-way video and audio transmissions simultaneously.
- The **chatroom** is a website or part of a website or an online service that offers communities a synchronous venue for discussing specific topics.
- **Webinar** is a seminar which is conducted over the WWW. It is a type of web conferencing. A webinar is “live” in the sense that information is conveyed according to an agenda, with a starting and ending time.

Computer-supported collaborative learning (CSCL) is one of the most promising innovations to improve teaching and learning with the help of modern ICT. Most recent developments in CSCL have been called e-Learning 2.0, but the concept of collaborative or group learning whereby instructional methods are designed to encourage or require students to work together on learning tasks has existed much longer.

The e-Learning environment

Most of the knowledge providers typically take existing educational materials (learning content), add various media, sequence them and use the “transferred” product in an online environment. Thereafter new or specifically tuned for e-Learning conditions contents are developed that gradually utilize capabilities of this technology. **Fig. 1** demonstrates categories of e-Learning and their relationship.

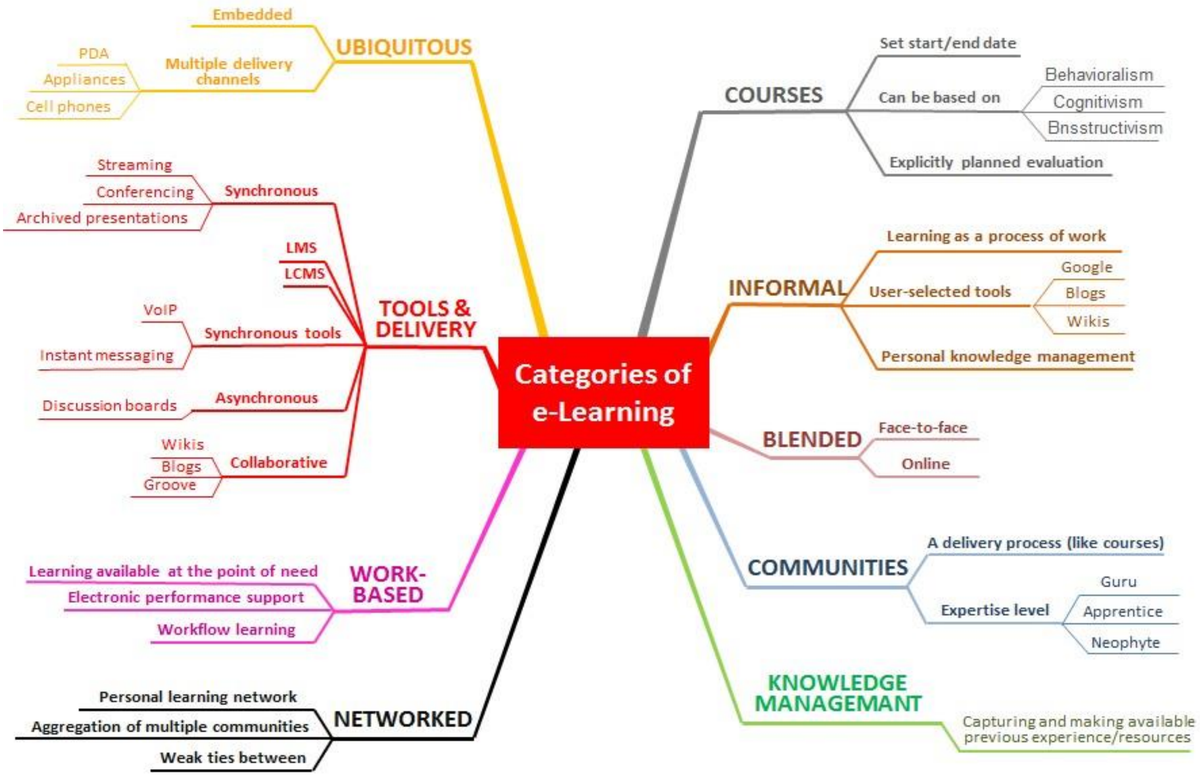


Fig. 1 e-Learning categories

The complexity of e-Learning operation requires an entirely new structure stretching between experts, teachers and the accumulated/archived knowledge base - learning content on one side and learners (target recipients) on the other side (**Fig. 2**). This mechanism is composed of two major parts:

a) the **learning content development** (LCD) engaged with production of the actual learning material;

b) the **learning management system** (LMS) organizing and recording all activities (of both learners and teachers), administrating the learning process, storing learning contents, facilitating interactions and feedbacks.

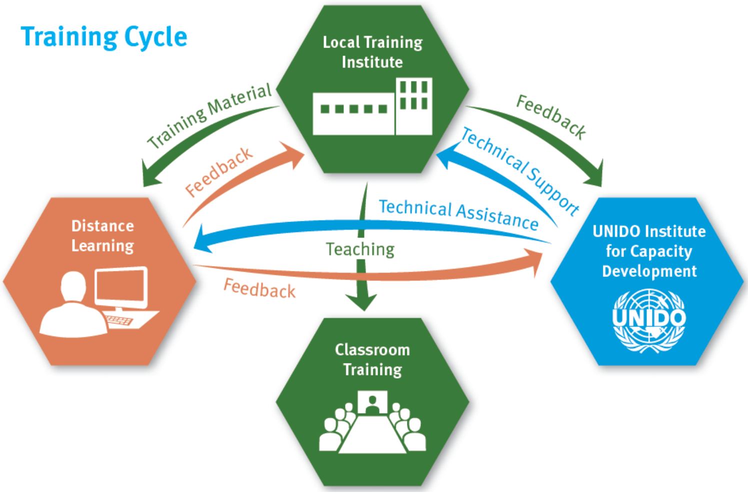


Figure 2: **eLearning** environment & training cycle

Learning content development

Although starting e-Learning services may be launched by using the existing knowledge base but converted into electronic formats, this does not suit current requirements for efficiency.

Learning content development within the leather value chain is an on-going challenge as it requires multidisciplinary team and resources. Due to the size of the leather sector to a date there are only few examples of e-Learning content development. Based on the Expert Group meeting focusing on the e-Learning in June 2016 in Mwanza/Tanzania, e-Learning is not used widely within the leather sector and institutions involved in the training have no only little knowledge with use of on-line training.

One of the core competencies of UNIDO is technology transfer. Although not an educational institution in of itself, UNIDO recognizes and fully embraces education and its multiple formats as a necessary and significant means to build technical capacity of it counterparts.

Lack of available learning content and training courses resulted in the development of on-line training courses and learning content (learning tools) which can be used by training institutions including industrial companies to train students either in face to face training with use of developed learning tools, for the self-learning or blended training.

UNIDO has started to build range of courses and learning content development (LCD) for the leather value chain:

i. Introduction to treatment of tannery effluents (5 modules)
ii. How to deal with hydrogen sulphide gas (module & test & certificate)
iii. First Aid (9 modules)
iv. Sustainable leather processing (Learning content under development)
v. Footwear pattern engineering (25 modules & 20 self-tests)

Course: Introduction to treatment of tannery effluents

The course supplement UNIDO paper "Introduction to the treatment of tannery effluents" (UNIDO 2011).

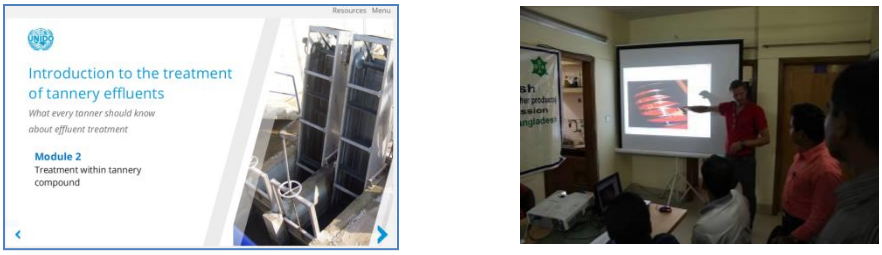
The animated presentation include the following chapters:

Module 1. **Load, norms, in-house treatment**
The aim of effluent treatment; pollution load and the main waste water quality parameters; typical discharge norms; general overview of the treatment of tannery effluents, segregation of streams, treatment of spent liming floats and treatment of chrome-bearing floats
Module 2. **Treatment within tannery compound**
Pre-treatment for discharge into CETP collection network, physical-mechanical (primary) treatment for discharge into municipal sewage.
Module 3. Sludge dewatering
Sludge thickeners, sludge pumps, filter press, centrifuge, belt filter press, flow-chart of physical-chemical treatment, sludge drying beds.
Module 4. Biological (secondary) treatment
Activated sludge, aeration devices, oxidation ditch, flow-chart of the biological treatment.

Module 5. Occupational safety and health (OSH) common effluent treatment plant (CETP) costing and management

Monitoring, OSH at work, CETP collection, CETP costing, flow-chart of fully fledged treatment;

Visual learning/training tool serves as a practical tool for UNIDO workshops in developing countries, mainly targeting leather technologists, tannery managers as well as decision makers of different profiles. It is also expected to help the staff of EPAs and members of NGOs in better understanding key issues and principles of the treatment of tannery waste waters.



Introduction to the treatment of tannery effluents

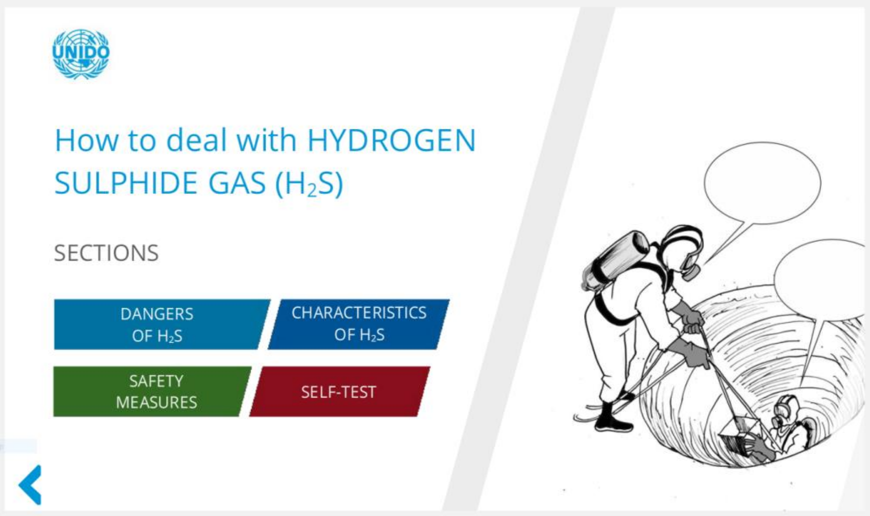
What every tanner should know about effluent treatment

Module 2
Treatment within tannery compound

Figure 3: Slide from Module 2 course Introduction to the treatment of tannery effluent and use of new training tools during face to face training

On-line Course: How to deal with hydrogen sulphide gas

The course How to deal with hydrogen sulphide gas is an example of self-learning material/content for wide use within the leather value chain. Similar course is used also for the oil industry on the commercial bases. due to the size of the leather sector it is unlikely that such approach will be widely used for the leather processing, however results and feedback from participants is very encouraging.



How to deal with HYDROGEN SULPHIDE GAS (H_2S)

SECTIONS

Figure 4: **Learning module for the course How to deal with hydrogen sulphide**

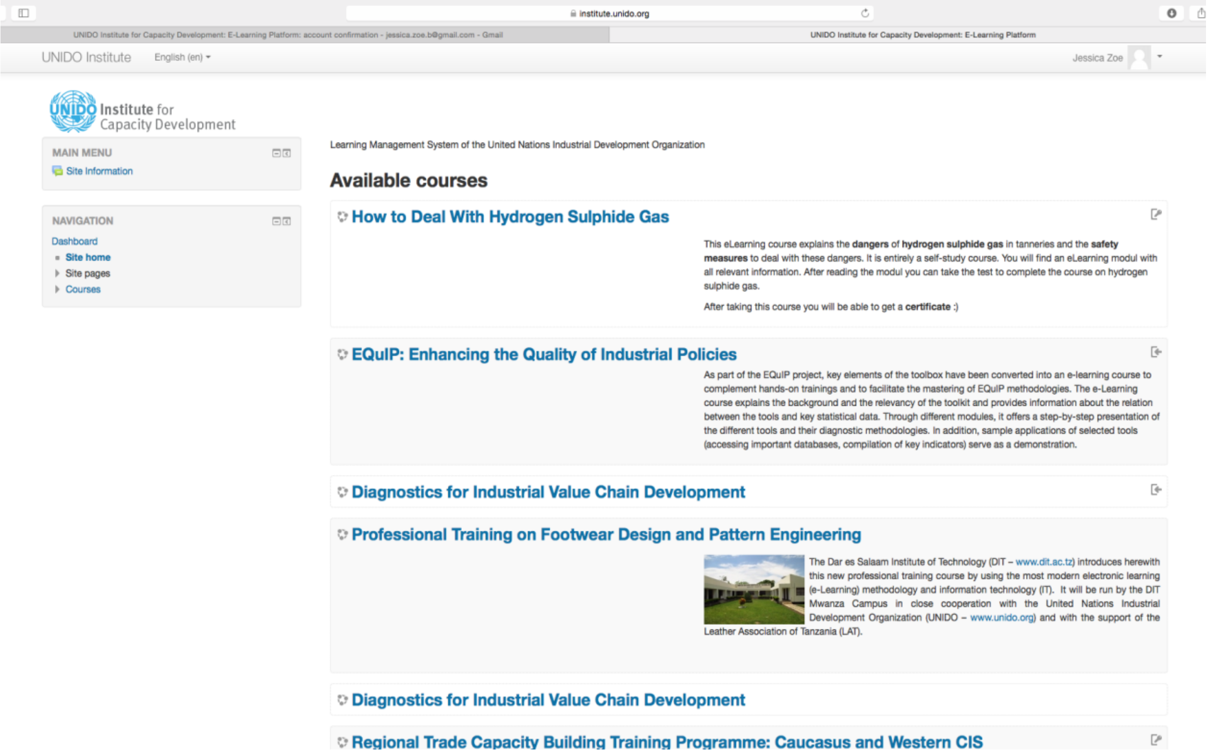
UNIDO has developed innovative e-learning training materials that can be used in different regions around the world. UNIDO's e-learning course on **"How to deal with Hydrogen Sulphide Gas"** is self-study, easy to use, and contains an animated visual training tool. The course complements UNIDO´s Safety Handbook on "How to deal with hydrogen sulphide gas in tanneries and effluent treatment plants", which is also available to download after enrolling in the course.

- This online course offers proper training related to dangers associated withH_2S;

- It has been specifically designed to help tanners, tannery and effluent treatment managers and operators understand the basic principles of how to deal with hydrogen sulphide gas;
- The course includes a test; after achieving a minimum score of 80 percent upon completion, participants will receive a certificate.

Course is possible to enrol in the UNIDO e-learning course hosted by UNIDO for Capacity development https://leatherpanel.org/content/unido-line-course-how-deal-hydrogen-sulphide-gas

After registration choose ´How to Deal with Hydrogen Sulphide Gas´ under ‘Available courses’ and enter enrolment key H_2Safety:



Learning Management System of the United Nations Industrial Development Organization

Available courses

How to Deal With Hydrogen Sulphide Gas

This eLearning course explains the **dangers** of **hydrogen sulphide gas** in tanneries and the **safety measures** to deal with these dangers. It is entirely a self-study course. You will find an eLearning modul with all relevant information. After reading the modul you can take the test to complete the course on hydrogen sulphide gas.

After taking this course you will be able to get a **certificate** :)

EQuIP: Enhancing the Quality of Industrial Policies

As part of the EQuIP project, key elements of the toolbox have been converted into an e-learning course to complement hands-on trainings and to facilitate the mastering of EQuIP methodologies. The e-Learning course explains the background and the relevancy of the toolkit and provides information about the relation between the tools and key statistical data. Through different modules, it offers a step-by-step presentation of the different tools and their diagnostic methodologies. In addition, sample applications of selected tools (accessing important databases, compilation of key indicators) serve as a demonstration.

Diagnostics for Industrial Value Chain Development

Professional Training on Footwear Design and Pattern Engineering

The Dar es Salaam Institute of Technology (DIT – www.dit.ac.tz) introduces herewith this new professional training course by using the most modern electronic learning (e-Learning) methodology and information technology (IT). It will be run by the DIT Mwanza Campus in close cooperation with the United Nations Industrial Development Organization (UNIDO – www.unido.org) and with the support of the Leather Association of Tanzania (LAT).

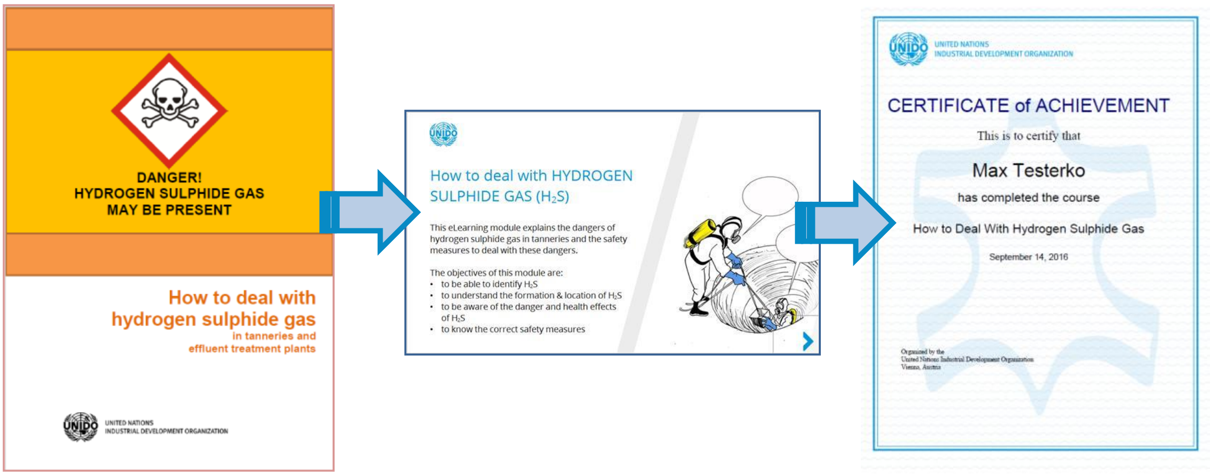
Diagnostics for Industrial Value Chain Development

Regional Trade Capacity Building Training Programme: Caucasus and Western CIS

Figure 5: **Learning module for the course How to deal with hydrogen sulphide**

Course content

1. Dangers of H_2S: Provides an overview of the health risks and physiological responses associated with the gas;
2. Characteristics of H_2S:This section covers risk areas in which hydrogen sulphide can occur, where it can be formed and under which conditions.
3. Safety measures:
   - Learn about preventive measures to decrease the risk of H_2S;
   - Understand how to detect and monitor H_2S exposure;
   - Know how to react to H_2S exposure, including how to use personal safety equipment.
4. Self test: a minimum score required is 80%
5. Certificate: After completing the test, participants can download their certificates



DANGER!
HYDROGEN SULPHIDE GAS
MAY BE PRESENT

How to deal with
hydrogen sulphide gas
in tanneries and
effluent treatment plants

UNITED NATIONS
INDUSTRIAL DEVELOPMENT ORGANIZATION

How to deal with HYDROGEN SULPHIDE GAS (H_2S)

This eLearning module explains the dangers of hydrogen sulphide gas in tanneries and the safety measures to deal with these dangers.

The objectives of this module are:

- to be able to identify H_2S
- to understand the formation & location of H_2S
- to be aware of the danger and health effects of H_2S
- to know the correct safety measures

UNITED NATIONS
INDUSTRIAL DEVELOPMENT ORGANIZATION

CERTIFICATE of ACHIEVEMENT

This is to certify that

Max Testerko

has completed the course

How to Deal With Hydrogen Sulphide Gas

September 14, 2016

Organized by the
United Nations Industrial Development Organization
Vienna, Austria

Figure 5: **Learning content for the course How to deal with hydrogen sulphide (a) technical handbook, (b) animated visual lesson (c) test (d) certificate**

e-Lerning courses developed by UNIDO has been used either for class-room trainings, self-learning and for the blended training courses in various countries. As only few on-line courses are available for the leather value chain, above mentioned courses are among first practically tested and used courses within the leather value chain.

CONCLUSIONS

One of the core competencies of UNIDO is technology transfer. Although not an educational institution in of itself, UNIDO recognizes and fully embraces education and its multiple formats as a necessary and significant means to build technical capacity of it counterparts.

Conventional training/teaching/learning methods and routinely suggested course durations, forms and arrangements suit neither today’s (to be) employees and industrial operations. Especially as manufacturing units are shifting from one region to other very fast. Similarly also training and retraining of workers and staff needs to be fast and efficient. Main concept of the new training is to use available technology to improve and increase learning efficiency by using and adopting e-Learning and appropriate tools.

Though no in-depth computer programming experience is required for building e- Learning content, all related software need some time to learn/practice utilizing their features and tools.

What are features of modern training/learning system?

- ✓ Flexible:
- ✓ modular
- ✓ complementary
- ✓ efficiency

Rapid development and especially information and communication technology (ICT) during recent years more and more also for development of training/learning material. With further development and especially new software various new training material, concepts and trainers aid have been developed, starting with knowledge bank up to more sophisticated animated and interactive training/learning courses and **eLearning** courses.

In short **e-Learning**isacomputerandelectronicnetworkenabledtransferofknowledge and skills:

a) availability of computers
b) Internet or Intranet connection with acceptable data transfer speed (for graphics) and access right to electronic learning resources;
c) learners basic knowledge and skills of handling hardware and using computer (programs),
d) availability of electronic learning materials such as courses, lessons, tests etc.

On one hand e-Learning offers flexibility (in terms of time, place and pace), on the other hand it requires all above conditions.

UNIDO has started to build range of courses and learning content development (LCD) for the leather value chain:

vi. Introduction to treatment of tannery effluents (5 modules)
vii. How to deal with hydrogen sulphide gas (module & test & certificate)
viii. First Aid (9 modules)
ix. Sustainable leather processing (course planned)

Main objectives of learning content development are:

- ✓ to provide access to up-date training programmes for training institutions especially in developing countries with limited resources;
- ✓ access to all students and trainees as access to education and training should be accessible to all and consequently it should lead to the development of the leather sector;
- ✓ same time with access to some region is not possible due to security issues and UNIDO is providing also assistance to such countries, on-line training and assistance is an opportunity to assist such regions;
- ✓ last but not least also it reduces costs of training.

Blended and on-line eLearning courses are accessible within www.leatherpanel.org portal or UNIDO Institute for Capacity Development and it is already used and tested in Tanzania by Dar as Salaam Institute of Technology (DIT), Mwanza campus.

To a date, participants from more than 170 countries use training material individually.

Coordination among various organizations and institutions in development of training programmes, is one option how to maintain required level of training reflecting requirements from industry for more effective and flexible training programmes. Cooperation and joint preparation of training material will lead to an efficient use of resources.

ACKNOWLEDGMENTS

The author appreciate the contribution from all authors of e-Learning material and content, Messrs. J. Buljan, F. |Schmel, Mr. F. Brugger from UNIDO Institute for capacity Development for all his support with LMS and courses, Common & Sense staff especially Mr. A Hoerfurther and Ms. C. Patschneider for all the work on this project, all users of e-Learning material for their valuable comments. Mr. J. Eischen for his proofreading.

Special thanks to all staff of Dar es Salaam Institute for Technology/Mwanza campus for active use of this new e-Learning approach and capability to adopt it in their activities.

REFERENCES

Selected UNIDO documents

1. Schmel F., e-Learning in the Leather-based Industries, 2012
2. Kral I., Professional training in leather based industries -Looking to the future 2016 for the 19th UITIC Congress Chennai/India
3. Report from the UNIDO Expert Group Meeting: “Knowledge Management Systems in Education and Training in the Leather Value Chain ”20-23 June 2016 Mwanza/tanzania

ROLE OF CSIR-CLRI IN SKILL INDIA INITIATIVE: ENRICHING PRIMARY LEVEL HUMAN RESOURCE THROUGH ARTISANAL SKILL DEVELOPMENT

Kanimozhi B*, Swarna V Kanth

Centre for Human and Organizational Resources Development (CHORD),
CSIR-Central Leather Research Institute (CLRI), Adyar, Chennai -600020, India,
Email:kanimozhi@clri.res.in, swarna@clri.res.in

CSIR-Central Leather Research Institute (CLRI) has catered to the artisanal training needs of the Indian leather sector since its inception through various avenues including the Leather Technology Mission. Today CSIR-CLRI, as a societal empowerment initiative, is hosting skill training programmes for the needy artisans below poverty line in different leather trades pan India with financial support from various institutions. The Institute has an outlay to train more than 10000 candidates in the next two years nurturing them to take up wage/self-employment. The paper focuses on the case study of skill development initiative taken up by CSIR-CLRI in association with several social organizations. CSIR-CLRI has successfully empowered 650 candidates in different leather trades during 2015-16 as part of the societal initiative. The study will cover a detailed analysis of the project including the skill training needs analysis, background of participants, eligibility criteria, implementation mechanism, project flow and critical phases. The trainees' perceptions on elements such as course material, infrastructure facilities and post-training assistance have been captured through feedback mechanism. Several statistical analysis tools will be employed to evaluate the results of training feedback. The primary objectives of the project include tapping the talent potential of Indian youth, improving productivity and improving quality of life of the needy. The outcomes of the training as against the objectives will be analyzed to come out with a model of success points and key areas for improvement. Thus a role model for skill development initiatives from CSIR-CLRI will be proposed for many such programmes to be taken up in future.

Keywords: skill development, societal empowerment, training needs

1. INTRODUCTION

India's leather industry has witnessed robust growth right from 1950, transforming from a mere raw material supplier to a value-added product exporter. Leather industry is the 8th largest foreign exchange earner of the country. Today, almost 50 per cent of India's leather business comes from international trade. India exported leather and leather goods worth USD 5.92 billion from April 2015 to March 2016.

The Indian leather sector currently employs over 3.09 million employees. It is estimated that approximately 3.7 million additional jobs will be created by 2022. The current industry trends including increased exports to high end markets thereby shifting towards mechanization. Skill gap in the sector is mostly at the entry level where the workforce lacks basic technical skills. Hence the major responsibility lies in endowing professional skill training to the workforce to improve the quality of workforce generated.

In the 12th five year plan, Government initiatives for leather sector skill development mainly focuses on placement linked skill development training with a plan to train around 2,00,000 unemployed manpower along with skill upgradation for trainers. The Human Resource Development (HRD) mission for leather sector targets skill development as well as technical development. The training proposed under the scheme is to be output linked where atleast 75% of those trained would be placed in the industry.

More than 90% of work force in leather sector is primary skill-oriented. ‘Leather Technology Mission’ of CSIR-Central Leather Research Institute (CLRI) focused on improving the effectiveness of the grass root artisans and productivity of the leather sector during the second half of the 90’s. Today CSIR-CLRI is hosting skill training programmes for the needy artisans below poverty line in different leather trades pan India. The Institute has an outlay to train more than 10000 candidates in the next two years through skill development programmes in association with several social organizations. These skill development programmes aim at nurturing the trainees to take up wage/self-employment. During 2015-16, CSIR-CLRI has trained around 650 artisanal candidates and has led to wage/self-employment.

The skill development model of CSIR-CLRI is one-of-its kind and has to be appreciated/ analyzed qualitatively as well as quantitatively to serve as a potential model for the upcoming skill development initiatives of the institute. The key objective of this study includes throwing light on the skill development model followed by CSIR-CLRI in 2015-16 to train the 650 artisanal candidates.

2. MATERIALS AND METHODS

The study assesses the skill development model/methodology followed by the institute through qualitative as well as quantitative approach. The skill development programmes in 2015-16 are analyzed in various aspects such as - the skill requirements and employment aspirations prevailing in the leather sector substantiating the need for the skill development training, objectives of the training, training model and mechanism involved in project implementation, the outcomes achieved in terms of placement

The outcomes of the training are analyzed quantitatively for the candidates covered in 2015-16 in terms of the number of candidates trained/placed region-wise and the demographic characteristics of the participants. The outcomes achieved through this project have been assessed by capturing the current status of the trainees and the improved quality of their life by means of wage/self-employment through interview/ on-field survey method.

The trainees' perceptions on the skill training have been captured through feedback mechanism. The elements such as course material, infrastructure facilities and post-training assistance are studied through survey administered to the candidates. The results will be utilized in improving the quality of the skill training imparted to candidates.

3. RESULTS AND DISCUSSION

3.1 Target trainees based on skill requirements in prominent clusters

Shop floor workers, machine operators and maintenance personnel constitute around 80% to 90% of the workforce in the lather processing or products industry. There is hardly any specialized short-term course to cater to the needs of these workers. The skill development efforts of CSIR-CLRI for the year 2015-16 covered the states of Tamil Nadu, Uttar Pradesh and West Bengal which have the highest incremental human resource requirements till 2022.

Table 1 – Incremental Human Resource Requirements by 2022

State (in '000s)	**Incremental requirement (in '000s)**
Tamil Nadu	1,948
Uttar Pradesh	1,206
West Bengal	325

Source: Report by National Skill Development Corporation

3.2 Sponsoring organization, eligibility criteria and courses offered

The skill development programmes during 2015-16 were organized in association with National Scheduled Castes Finance and Development Corporation (NSFDC). The programmes focusses on improving employability of Scheduled Castes youth belonging to DPL (double below poverty line – Rs.98,000/- for rural areas and 1,20,000/- for urban areas). The eligibility criteria for the candidates with respect to age: 18-50 years of age and qualification with minimum 5th standard (pass) for the 35-day/ 60-day programme.

3.3 Objective of skill training

- To provide skill development training that would lead to increase in employability and productivity of the workforce for the Indian Leather sector
- To train the needy artisans in state-of-the-art technology cum infrastructure
- To create employment opportunities for the candidates through skill training, in the industry, to work or to start their own micro enterprises with great results along with giving preference to women beneficiaries
- Imparting market based skills along with technical skills on shop floor operations of Leather Processing Technology, Footwear Manufacture, Leather Goods and Garments to youth
- Focus on overall personality development of the trainees and production of technically better products for their effective integration with the organized sector in the Leather industry
- To enable the trainees to gain hands-on learning experience beyond the common learning programs and help them to spread and sustain a technology culture through exposure to global best practices

3.4 Training Model and Mechanisms Involved in Project Implementation

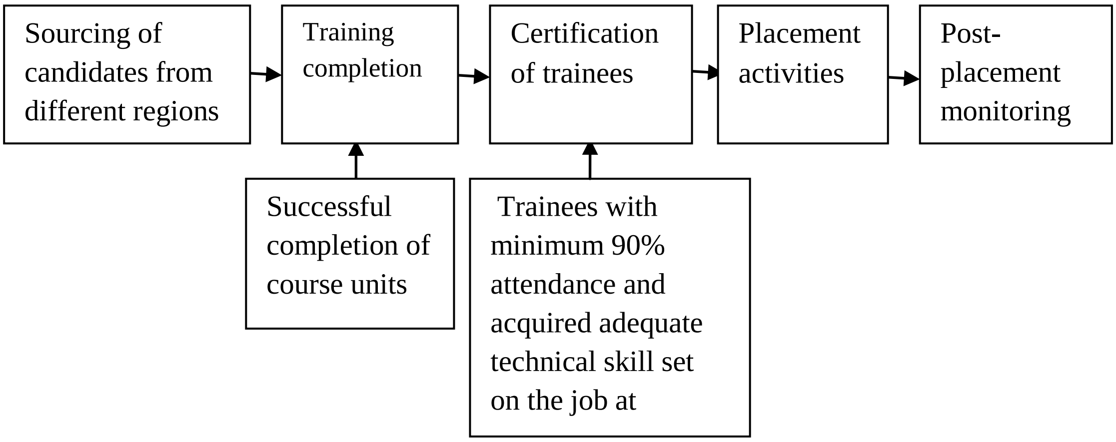


Figure 1 – Training Model

3.4.1 Training Curriculum

The curriculum of the training is standardized and as per standard acceptable to the industry. CSIR-CLRI awarded a proficiency certificate to all those trained under the scheme. CSIR-CLRI’s model of imparting skill training will be in tandem with the enormity of the skill needs in the industry and the variety of existing strengths that can be leveraged.

3.4.2 Identification of trades

The trades covered are those employed in the entire value chain from leather processing to finished products, such as Leather Processing Technology (Tanning, Post-tanning and Finishing – each module for 60 days) Footwear Manufacture (cutting and clicking, closing and stitching, chappal-making – each module for 35 days), Leather Goods and Garments (cutting and clicking, assembling and stitching – each module for 35 days).

3.4.3 Identification/selection of trainees

Sourcing and mobilization of candidates was primarily carried out through State SC Corporations/ State Channelizing Agencies/ NGOs/ leather industry associations. Selection process is demand driven. The interested candidates who apply for the programmes will be initially screened based on the eligibility criteria. Those who satisfy the eligibility criteria will be called for a counselling process and they will be counselled on the future prospects after skill training in different areas. Only those who seriously wish to acquire skill and get placement in the leather industry will be considered for selection.

3.4.4 Implementation

CSIR-CLRI’s role is to provide technical training, support, monitoring and concurrent evaluation. CSIR-CLRI also outsourced the training amongst its regional centers for extension and development (RCED). Periodic monitoring and assessment of the training will be conducted by experts of CISR-CLRI at the Head-Quarters as well as regional centres and final authenticated certification is provided by CSIR-CLRI.

3.5 Training coverage pan India

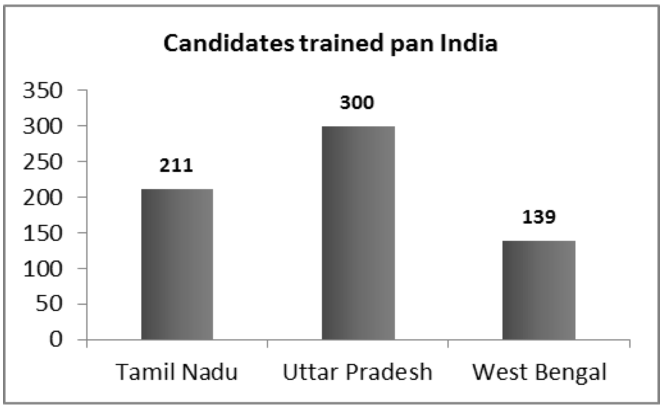


Figure 2 – Candidates trained pan India

The primary need that was felt in the different leather and leather product clusters in Uttar Pradesh, Tamil Nadu and West Bengal is that availability of abundant supply of skilled labor. The positioning of these clusters in the global value chainis such that their competitive advantage is drawn out by nurturing valuable primary level human resource to the maximum extent possible. The supply of skilled labor with formal certification in line with the national agenda is the need of the hour. The Kanpur leather cluster is increasingly getting integrated in a global manufacturing and distribution chain and hence witnessed the maximum coverage of candidates (300 nos.).

3.6 Demographic analysis of participant profile

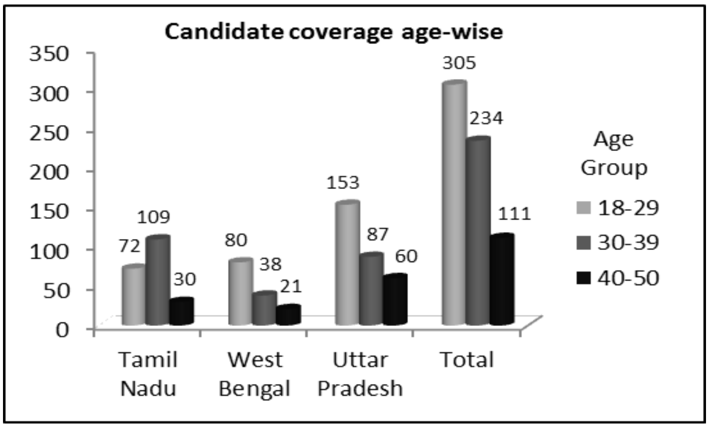


Figure 3 - Coverage of candidates age-category wise

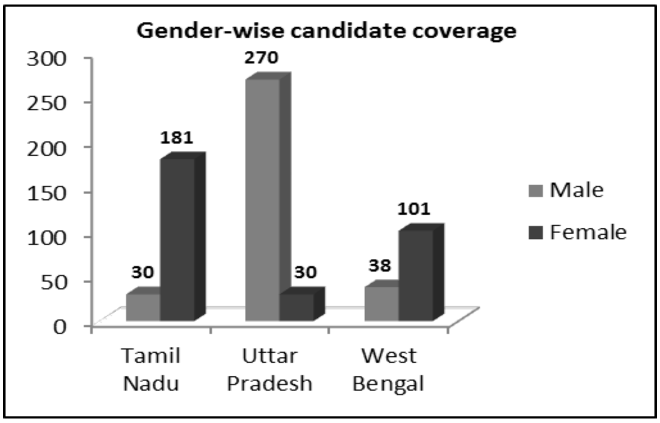


Figure 4 - Gender-wise candidate coverage

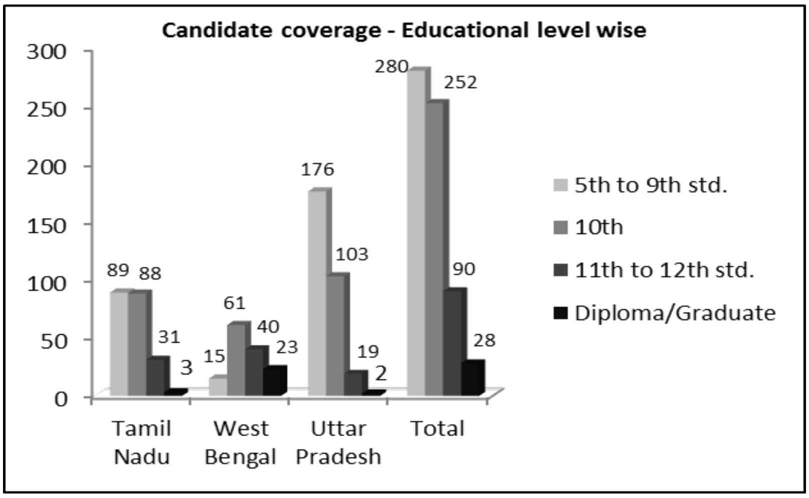


Figure 5 - Education level wise candidate coverage

The Fourth Annual Report on Employment and Unemployment 2014 states that in India 13 in 100 are unemployed in the 18-29 age group. Majority of the participants who were sourced and mobilized for skill training belonged to the 18-29 age group. To make this skill empowerment initiative a model programme for women empowerment, the prime focus was on garnering women candidates. Around 48% of the total candidates trained were women. Low educational status is quite prevalent among the candidates with 43% of candidates with educational level of 5th to 9th standard and 38% of candidates who have studied upto 10th. 4.3% of the total candidates were Diploma/Degree holders from a low economic background who decided to take up a career in leather sector with the aid of skill training.

3.7 Outcomes of training – Placement Record

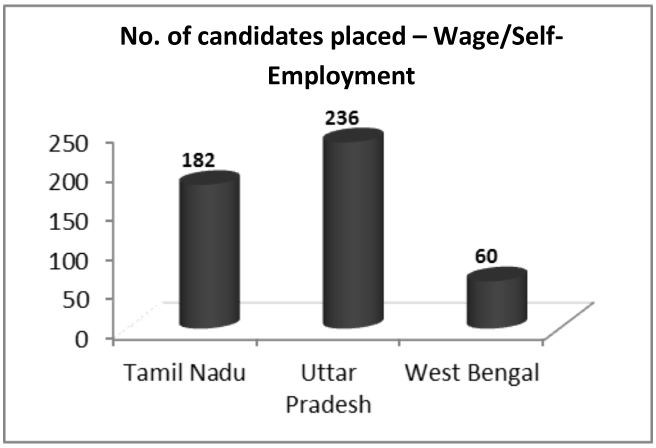


Figure 6 – Number of candidates placed

The Institute owing to its bondage with the industry has placed 478 candidates in wage/self-employment in the states of Tamil Nadu, Uttar Pradesh and West Bengal. 3 candidates from Chennai are engaged in CSIR-CLRI itself as trainers for subsequent batches of skill training at a remuneration of Rs.15,000/- per month.The average salary of wage-employed candidates considering all the three centres in Rs.9400/- with the highest average salary being Rs.13,000/- (in Chennai). Around 28 candidates trained from Perambur Cluster in Chennai have formed small self-help groups within themselves and are earning at an average of Rs.10,000/- per month by taking up small job works. Thus the skill training has paved way to change the outlook of trainees and be self-sustained.

3.8 Training Feedback

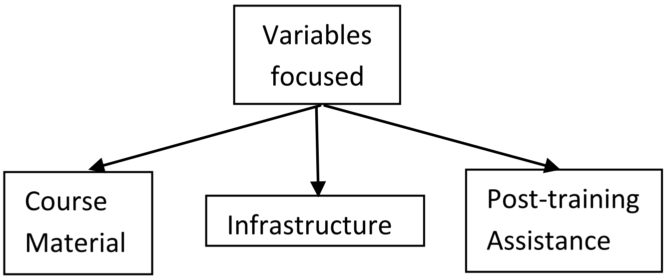


Figure 7 - Focus variables of feedback

The training feedback captured the trainees’ perception on the elements such as course material, infrastructure and post-training assistance. The mean scores from descriptive statistics revealed course material as the top scoring element of training followed by infrastructure (mean score of 11.23) and post-training assistance (mean score of 9.46). This inference ensures that superior quality of training imparted at CSIR-CLRI. Friedman test revealed the statistically significant attributes of each element of training. With respect to course material, clarity of course structure (theory and practical parts) (rank - 2.81) and periodic monitoring during the course of skill training (rank - 2.63) are the top two ranking attributes of course material. Adequacy and quality of faculty (rank - 2.08) and quality of infrastructure and tools (rank - 2.07) are the top two ranking attributes pertaining to Infrastructure element. This inference substantiates the point that the trainers at CSIR-CLRI impart the various nuances involved in each module with respect to skill training. The feedback analysis also revealed that trainees are the trainees are highly satisfied with the timely and orderly payment of stipend amount to them (rank- 2.09).

The different groups of candidates pertaining to demographic variables of age, gender and educational qualification did not show significant difference in their mean scores for the elements of training analyzed through feedback. This is evident from the significance values obtained from the independent sample t-test and Analysis of Variance (ANOVA) test where the significance values for these demographic variables vs. training elements are greater than 0.05. Hence it is inferred that the skill training programme has been structured to cater to suit the skill requirements of candidates from different demographic categories.

4. CONCLUSIONS

This paper mainly focuses on analyzing the model of skill development followed by CSRI-CLRI and implementation mechanism employed. The study indicates that the organization has oriented the best of its efforts towards nurturing a skill development model to foster rich societal empowerment initiatives. The perception of the skill trainees also reveal that they are satisfied with the quality of training imparted at CSIR-CLRI. The skill training also incorporates efforts to keep the trainees updated on the dynamic changes in the industry environment and job market. Thus CSIR-CLRI will utilize its technical expertise to touch the lives of common man through technological training thereby enriching primary level human resource.

5. Acknowledgements

The authors express their deep sense of gratitude to Dr.B.Chandrasekaran, Director, CSIR-Central Leather Research Institute (CLRI), who has provided his continuous support and guidance for the skill development efforts of CSIR-CLRI.

The authors convey their heartfelt thanks to Dr.R.K.Singh, Chairman cum Managing Director, National Scheduled Castes Finance and Development Corporation (NSFDC), for providing CSIR-CLRI with the opportunity to serve the needy society.

The authors express their sincere gratitude to the members of CSIR-CLRI, NSFDC, candidates who have undertaken the skill training at CSRI-CLRI and all members who were involved in the successful completion of the project.

6. REFERENCES

1. National Skill Development Corporation (NSDC) (2009). Human Resource and Skill Requirements in the Leather and Leather Goods Sector (2013-17, 2017-22). Retrieved from http://www.nsdcindia.org/sites/default/files/files/Leather-2009.pdf
2. National Skill Development Agency (NSDA) and the National Skill Development Corporation (NSDC) (2014). Youth Empowerment through Skill Development. http://www.nsdcindia.org/sites/default/files/files/pdf/SDReport.pdf
3. Ministry of Labour and Employment (Government of India) (2014). Report on Employment-Unemployment Survey. Retrieved from http://labourbureau.nic.in/Reportfinal.pdf
4. National Skill Development Corporation (NSDC). (2016). Retrieved from http://www.nsdcindia.org/
5. Central Leather Research Institute (CLRI). (2016). Retrieved from http://www.clri.org/

INDO-ETHIOPIAN ALLIANCE FOR TRANSFORMATION OF ETHIOPIAN LEATHER SECTOR

Wondu Legesse* and B Chandrasekaran*

Leather Industry Development Institute, Akaki Kality, Addis Ababa, Ethiopia
CSIR-Central Leather Research Institute, Adyar, Chennai-600 020, India

Leather has played an important role in the development of civilizations. Today leather products are considered to be one of the most important consumer products. Leather and leather products industry is one of the strategic sectors of Ethiopia in view of economic growth, foreign exchange and employment generation. The raw material resource is one of the strength points of Ethiopia and the Ethiopian High Land sheep skins are known for their quality to produce all kinds of leather products, particularly their suitability for making niche products such as glove leathers. Ethiopia has been consistently figuring in the list of top 30 countries contributing to the raw material base for the global leather industry. Ethiopian government has been taking proactive measures to facilitate forward integration and value addition in leather sector. The Federal Democratic Republic of Ethiopia is aiming for a giant leap in leather and leather products by providing favourable policy environment and strategic incentives for the sectors.

CAPACITY BUILDING ETHIOPIAN LEATHER SECTOR:

Every development needs capacity power house from all participants of the sector. For the leather sector the capacity building program was mainly focused in two areas. These are Institutional Capacity Building Program, which was planned to build the intuitional capacity of Ethiopian Leather Industry Development in order to enhance the support capacity for the sector. The other capacity building program was to enhance the capacity of the sector main players, Tanneries and Shoe manufacturers. These two capacity building programs are addressed by Twinning and Benchmarking Programs.

BENCHMARKING PROGRAMME

The Ethiopian government considers that the leather industry, being the largest manufacturing industry has the potential to contribute significantly to the export earnings of the country on one hand and employment opportunities on the other. Hence, it is trying to catalyze the growth of the industry through policy interventions and intensive technology up gradation programmes through bench marking projects for tanning and footwear industries. CSIR-Central Leather Research Institute (CSIR-CLRI) did Benchmarking - Technology up gradation of tanning sector and the programme for footwear sector was carried out by Footwear Design and Development Institute (FDDI) of India. Phase I of Benchmarking programme was undertaken between March and September 2010. CSIR-CLRI deputed project team to undertake technology up gradation programme at selected tanneries in Ethiopia. After the successful completion of first phase Benchmarking programme, second phase programme was carried out in selected eleven tanneries for the period between January and August 2011. The benchmarking programmes were leading to self-sustainability of the Ethiopian tanneries in terms of new products development, competence building in the areas of research & development, technical up gradation, Product & Quality standardization and productivity enhancement with system formulation and implementation for production of finished leathers for export. Subsequent to the successful implementation in capacity building of Ethiopian tanneries, Govt of Ethiopia banned the export of intermediate processed leathers, exports of finished leather and leather products only were permitted.

The various action modules covered under the benchmarking programme are as follows:

- Selection of new products/Development or standardization of process technology/ Market linkage / Production
- Up gradation of lower ends and full exploitation of splits
- Strengthening of technological capabilities for the production of *glove and suede leathers*
- Strengthening of tannery machinery system
- Training of Machine operators (buffing and polishing)
- Ensuring implementation of an integrated system for efficiency & profitability enhancement in tanneries
- Capacity building in the finished leather production
- Article specific quality control, machine operation, planning

CAPACITY BUILDING ETHIOPIAN LEATHER INDUSTRY DEVELOPMENT INSTITUTE: TWINNING PROGRAMME

Leather Industry Development Institute (LIDI) has been established by the Govt. of Ethiopia primarily to serve the leather and products sectors. Through LIDI, Ethiopian Government had executed Benchmarking - Technology Upgradation of Ethiopian Leather and Leather Products sector. In view of the new national policy on leather and leather product sectors, the support systems in terms of technology supply, manpower development in Ethiopia are needed to be in place. The role to be played by LIDI in this context are much crucial. In order to realize the national goals and vision, LIDI’s capability and capacity need to be enhanced significantly. The transformation of LIDI to be capable of serving the industry and ultimately to bring about the envisaged growth of the leather and leather products sectors, a project to Twin the capabilities of CSIR-CLRI by LIDI was envisioned. The TWINNING project had been structured, planned and executed taking into account the principal objective of transforming LIDI. The ultimate transformation would enhance LIDI’s capability to offer all the needed services and support for the whole leather value chain. The major objectives of the Twinning project are as follows.

- Creating and providing intellectual and skilled manpower to cater to the requirements of the industry
- Providing technical support in all the spheres of leather and leather product sectors
- Providing services to the industry such as testing, certification and establishing norms or standards
- Forecasting the global market dynamics and preparing the Ethiopian leather and leather products sectors to meet the changing requirements

- Creating functional tripartite linkage among the University, R&D/laboratories and industry to start real time activities in research and training during the twinning period for strengthening B.Sc programme and commencing M.Sc. and PhD programmes in leather.
- To act as a nodal centre for training the trainers who in turn will serve the TVET centres
- To promote and support the growth of SME in leather and leather products sector through various entrepreneurship development programmes

CSIR-CLRI had given a comprehensive proposal for enabling LIDI to become a globally competent centre. The twinning programme was carried out for a period of three years between 2011 and 2014. The major areas covered under twinning are strengthening academic programmes of LIDI, providing industrial consultancy in the areas of leather and products through applied research, establishing testing services and human resource development for the product sector through vocational programmes.

Footwear Design and Development Institute (FDDI) had been a partner to carry out activities related to the areas of footwear and leather goods. A total of about 600 man-month interventions had taken place for carrying out the activities under twinning project.

Summary on Accomplishments of Twinning Programme Phase I

To capacitate LIDI to undertake and carry out research and development activities in leather, leather products and allied areas

Accomplishments

- A state-of-the-art laboratory established
- Two product development centres are established both for the footwear and articles.
- Joint R&D programs in leather and products undertaken
- Academic projects carried out under M Sc programs
- Research works are carried out through Ph D programmes

Outputs:

- One paper presented in Turkey IULTCS (2013)
- Two papers presented in Asia congress held in Japan (2014)
- About 10 publications made in peer reviewed scientific journals
- Two patents filed
- Spin off projects (a. Study of histology of Ethiopian hides and skins: ETB 2 million; b. Multifunctional Fatliquor from indigenous source: ETB 0.8 million from MoS&T) secured

To capacitate LIDI to undertake industrial consultancy activities in leather, leather products and allied areas

Accomplishments

- Consultancy projects in leather (M/s Sheba Tannery), in products (M/s Anbesa, M/s ELICO, M/s Sheba) have been taken up and completed

- Training of manpower for M/s Pittards completed

Outputs:

- As many as five industrial units benefitted
- About 15 personnel (of LIDI) were trained on consultancy in leather and leather products areas
- One consultancy service (post-twinning) has been taken up in ELICO by Leather Technology Directorate
- Consultancy services have been taken up in product units too

To capacitate LIDI to establish/strengthen academic (B Sc) and skill development program (TVET)

Accomplishments

- Academy - Research linkage established between LIDI on one part and Addis Ababa institute of Technology, College of Veterinary medicine & agriculture and Addis Ababa Science and Technology University on the other
- B Sc program curriculum reviewed and B Sc program conducted for three years
- First degree program for footwear and leather products was started with Addis Ababa Science and Technology University.
- TVET (leather and goods & garments) curriculum reviewed, syllabus prepared and teaching and learning materials prepared

Outputs:

- LIDI capacitated in conducting the B Sc program in Leather and Footwear Technology
- LIDI also capacitated in conducting TVET programs

To capacitate LIDI to provide testing and analytical services with excellence of international position

Accomplishments:

- CLRI facilitated the modernization of testing and analytical laboratory
- Series of advanced training programs conducted at LIDI and at CLRI

Outputs:

- Physical testing and chemical analysis laboratory capacitated to perform to meet international requirements

To capacitate LIDI to develop built-in mechanism for continual improvement

Accomplishments:

- A quality management system in accordance to ISO 9001 has been designed and implemented

- Organization restructured
- Training provided to enhance administrative capability of LIDI

Outputs:

- New structure of organization is in place
- This led to the basis for organization restructuring many similar organizations
- LIDI - world's first leather institute certified with ISO 9001
- Biometric system introduced in LIDI

To improve the overall management and functional capability of LIDI

Accomplishments:

- Training in internet and intranet provided
- Video-conference facility established
- LIDI website modified
- Intranet established in LIDI
- Software for purchase developed
- Personnel trained on leadership skills and soft skills

Outputs:

- LIDI is internet and intranet capable
- Video-conference facility will enhance the long distance communication and discussion
- The overall soft skills ability of LIDI top management personnel enhanced

Twinning Programme Phase II

After the successful completion of Phase I Twinning project, second phase of twinning project between CSIR-CLRI and LIDI commenced from June 2015. The focus on the Phase II twinning project had been to strengthen Environment Engineering, consultancy and technology development & transfer activities.

ALLIANCE: WAY FORWARD

CSIR-CLRI and LIDI Twinning is a great partnership that proves to be a fitting model of win-win, which built not only the collaboration between two institutes but also two countries. The alliance established between LIDI and CSIR-CLRI is a role model for capacity building of institution and industry. The ties between LIDI and CSIR-CLRI are expected to grow from strength to strength for the sustainable development of global leather sector.

GRAP O-42

DEVELOPMENT OF AN INTERNATIONAL PROFICIENCY TESTING BY INTERLABORATORY COMPARISON APPLIED TO PHYSICAL AND CHEMICAL TEST METHODS FOR MINERAL TANNED LEATHER 2016

Carlos Amador Meza Moya

Department of Quality Management, CIATEC, A.C. Omega 201, Industrial Delta, C.P. 37545, León, Guanajuato, México

**Email: cmeza@ciatec.mx*

Given the environment of global competition for markets, the leather industry and footwear must be able to demonstrate the confidence it has on the quality of materials and products that are marketed, so that it must be supported by third-party laboratories using quality assurance mechanisms that give customers greater confidence, objectivity, transparency, compliance with the international system of units and especially to achieve greater accuracy and traceability to reference materials available.

In this context, one of the problems experienced by a leather testing laboratories in the world has to do with the inability to demonstrate expertise in international testing methods determined by third-party organizations (proficiency testing providers to the industry leather), why the business opportunities are limited because they can not prove competitive advantages (technical expertise for carrying out mechanical tests materials leather-footwear) over other testing laboratories.

Through the United Nations Development Program, supported by the governments of Mexico (AMEXID) and Uruguay (AUCI) and the participation of more than ten countries in America and Europe has developed a project for two international rounds of proficiency testing by interlaboratory comparison according to the guidelines of the ISO / IEC 17043:2010, in order to demonstrate competence in carrying out test methods for mineral-tanned leathers and increase the competitiveness of the leather-footwear industry sector.

1. INTRODUCTION

The interlaboratory comparison consists in testing the same samples by different laboratories and in comparing the results. They are a major element in ongoing quality assurance programs.

These objectives are usually pursued:

- ✓ Demonstrate consistency of results between laboratories.
- ✓ Determine the performance of individual laboratories for specific tests or measurements.
- ✓ Help identify problems in laboratories and initiate actions to remedy these problems.
- ✓ To establish the effectiveness and compatibility tests or new measurement methods and similarly to monitor established methods.
- ✓ Identify differences between laboratories.

- ✓ To determine the performance characteristics of a method.
- ✓ Assign values to the material of reference and assess whether they are suitable for use in specific procedures or specific tests.

In practice, it consists in:

Sending to a sufficient number of laboratories a series of samples as similar as possible;

Running a series of tests by all participating laboratories;
Determining a reference value to be found for the test results;
Evaluating the difference between the results of each laboratory and the reference value and concluding a level of confidence in the outcome of the test.

The second round of the *International Proficiency Testing by Interlaboratory Comparison Applied to Physical and Chemical Test Methods for Mineral Tanned* was organized and coordinated by the ***Center for Applied Innovation in Competitive Technologies CIATEC, A.C***. of Mexico, in collaboration with the ***Technological Laboratory of Uruguay LATU***. The testing itself was being carried out from June through August 2016.

The testing program was performed according to a simultaneous sample test arrangement divided by interlaboratory comparison, in accordance to protocol URU / 13 / 001-1

2. MATERIAL AND METHODS. PARTICIPANTS

Twenty laboratories participated, out of which 17 are in the American continent and 3 in the European continent:

- Bader International, Uruguay.
- Calzado Flexi, México.
- Centro de Diseño y Manufactura del Cuero SENA, Colombia.
- Centro de Innovación Aplicada en Tecnologías Competitivas CIATEC A.C., México.
- Centro de Innovación Tecnológica del Cuero, Calzado e Industrias Conexas CITECCAL, Perú.
- Centro Tecnológico do Calçado de Portugal CTCP, Portugal.
- Centro Tecnológico do Couro e Meio Ambiente, SENAI, Brasil.
- Centro Tecnológico para las Industrias del Calzado, Cuero y Afines CEINNOVA, Colombia.
- Eagle Ottawa by Lear, México.
- El Pequeño Curtidor de León PCLab, México.
- Escuela de Ingeniería de Igualada Cátedra A3, Universitat Politecnica de Catalunya, España.
- First Lab, México.
- Grupo Atlas Ltda, Colombia.
- GST AutoLeather, México.
- Instituto de Tecnología Industrial del Cuero INTI, Argentina.
- Instituto Tecnológico del Calzado y Conexas INESCOP, España.
- Laboratorio Tecnológico del Uruguay LATU, Uruguay.

- Paycueros, Uruguay.
- SADESA, Argentina.
- Zenda Leather, Uruguay.

Material and methods. Tests carried out in this inter-laboratory comparison:

- ISO 3376 IULTCS / IUP 6, Leather - Physical and mechanical tests - Determination of tensile strength and percentage extension. Third edition 2011-12-15.
- ISO 3377-2 IULTCS / IUP 8, Leather - Physical and mechanical tests - Determination of tear load - Part 2: Double edge loom. First edition 2002-12-15.
- ISO STANDARD 4045 IULTCS / IUC 11 Leather - Chemical tests - Determination of pH. Second edition 2008-02-15.
- ISO 5398-1 IULTCS / IUC 8: 1, Leather - Chemical determination of chromic oxide content – Part 1: Quantification by titration. First edition 2007-08-01.

Material and methods. Methodology.

Two variations were followed, one for physical tests and a second one for chemical tests

Physical tests methodology:

- Leather tanned sheets are selected
- Minimum sample size per participant defined; n = 10 specimens (taken in such a way that all participants have specimens of all sheets and all positions)
- Minimum number of laboratory participants ascertained at 15
- Value assigned to the leather sample as robust median x * according to algorithm A of Annex C of the ISO 13528 *Statistical methods for use in proficiency testing by interlaboratory comparisons*.
- Variability of the test s * determination as algorithm A of Annex C of ISO 13528 *Statistical methods for use in proficiency testing by interlaboratory comparisons*.
- Evaluation value z or z ' determination (in case the uncertainty "u" of the value assigned to the test item is significant with respect to s)

It should be noted that this type of testing program will always depend significantly on the homogeneity of the leather test item. It is therefore important to have at least samples of size n = 10 with no less than 15 participants.

Chemical tests methodology:

- Tanned leather mechanically crushed and homogenized.
- Value assigned to the item by a reference laboratory.
- Variability of the test determination. It is recommended to carry out a multi-level r and R study to establish the precision of both repeatability and reproducibility, since these tests do not depend on the homogeneity of the sample.

- Evaluation value z or z ' determination (in case the uncertainty "u" of the value assigned to the test item is significant with respect to s)

Material and methods. Final Schedule of the Interlaboratory Comparison of Test methods, program

Activity-date 2016

Planning and protocol preparation activities. February-March
Invitation. April
Preparation of the leather sheets to be tested. April-May
Receipt of registration applications. April-May
Performing the tests. June-August
Analysis of the results and preparation of the report. September
Delivery of results to the participants. October
Program Qualification. October

Material and methods. Test item definition.

Leather tanned to the mineral

The values assigned to the test item were determined as the robust mean of the participants according to the models of section C.3.1 using the algorithm A of Annex C of ISO 13528 *Statistical methods for use in proficiency testing by interlaboratory comparisons.*

3. Results and Discussion. Results reported by participants.

Asample table of the results reported in herein shown:

			Physical and mechanical test level 1			Physical and mechanical test level 2			Chemical Test	
Laboratory Code	Enviorementas condition		Tensile Strength	Percentage Extension	Teard Load	Tensile Strength	Percentage Extension	Teard Load	pH	Chromic Oxide Content
	°C	% HR	N/mm²	%	N	N/mm²	%	N		%
L105	21	56	21,66	78,56	NP	20,33	61,18	NP	3,483	NP
L106	23	50	23,09	65,45	192,00	20,04	49,94	116,40	NP	NP
L107	23	50	23,30	57,10	184,80	20,30	43,20	105,20	3,535	3,705
L108	23	50	24,41	62,55	177,23	20,46	51,09	108,06	3,500	3,700
L109	23	50	24,32	50,60	192,30	20,62	41,88	125,09	3,440	NP
L110	20	50	23,26	57,16	NP	18,56	44,72	NP	3,528	3,423
L111	23	50	24,58	60,55	188,25	21,75	45,82	114,02	3,510	3,613
L112	20	65	22,35	56,25	179,93	20,44	45,52	108,95	3,490	3,780
L113	24	38	24,15	63,45	191,80	20,18	51,32	116,20	NP	NP
L114	23	50	23,71	65,84	214,04	19,07	49,91	121,28	3,628	3,588
L115	23	50	22,98	67,88	199,34	17,64	47,76	119,73	3,453	3,575
L116			18,80	66,36	186,80	15,49	52,07	113,20	3,578	np
L117	23	50	24,64	66,90	165,83	19,77	54,70	99,12	3,773	3,84
L118	23	50	23,99	59,82	158,47	20,02	48,55	96,97	3,763	3,700
L119	23	53	22,94	60,28	178,20	18,87	58,26	104,10	NP	NP
L121	21	65	NP	NP	186,00	NP	NP	110,40	3,455	3,275
L122	22	50	24,35	60,89	157,97	20,82	51,55	94,19	3,593	NP
L123	20	50	27,16	62,30	191,80	21,90	50,04	117,15	4,780	NP
L124			24,57	64,90	198,50	20,33	52,20	103,00	3,600	NP

Note: NP mean non participant

Results and Discussion. Evaluation and analysis.

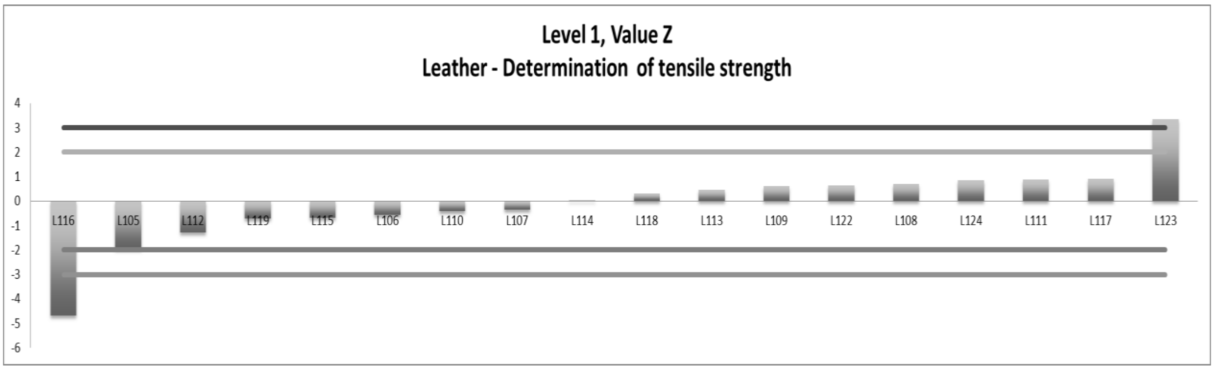
The evaluation of the results was performed using the z-values according to *ISO / IEC 17043 Conformity assessment - General requirements for proficiency Testing 2010*

Sample evaluation table per participant:

Laboratory CODE	Tensile strength Level 1, Leather	Percentage Extension Level 1, Leather	Tear load Level 1, Leather
L105	-1,94	**3,36**	SC
L106	-0,57	0,64	0,51
L107	-0,37	-1,09	-0,11
L108	0,70	0,04	-0,76
L109	0,61	-2,44	0,53
L110	-0,41	-1,08	SC
L111	0,86	-0,38	0,19
L112	-1,28	-1,27	-0,53
L113	0,44	0,23	0,49
L114	0,02	0,72	2,40
L115	-0,68	1,14	1,14
L116	**-4,69**	0,83	0,06
L117	0,91	0,94	-1,74
L118	0,29	-0,53	-2,37
L119	-0,71	-0,43	-0,68
L121	SC	SC	-0,01
L122	0,63	-0,31	-2,41
L123	**3,33**	-0,01	0,49
L124	0,85	0,53	1,07

Note: bold value means unsatisfactory, Underlined value means questionable
Normal values means satisfactory

To make possible a better first comparison of results, some graphs were prepared, like the one given here:



Summary of the evaluation:

Level 1, Leather - Physical and mechanical test

Laboratory CODE	Tensile strength N/mm^2	Percentage Extension %	Tear Load N
L105	Satisfactory	Not satisfactory	SC
L106	Satisfactory	Satisfactory	Satisfactory
L107	Satisfactory	Satisfactory	Satisfactory
L108	Satisfactory	Satisfactory	Satisfactory
L109	Satisfactory	Questionable	Satisfactory
L110	Satisfactory	Satisfactory	SC
L111	Satisfactory	Satisfactory	Satisfactory
L112	Satisfactory	Satisfactory	Satisfactory
L113	Satisfactory	Satisfactory	Satisfactory
L114	Satisfactory	Satisfactory	Questionable
L115	Satisfactory	Satisfactory	Satisfactory
L116	Not satisfactory	Satisfactory	Satisfactory
L117	Satisfactory	Satisfactory	Satisfactory
L118	Satisfactory	Satisfactory	Questionable
L119	Satisfactory	Satisfactory	Satisfactory
L121	SC	SC	Satisfactory
L122	Satisfactory	Satisfactory	Questionable
L123	Not satisfactory	Satisfactory	Satisfactory
L124	Satisfactory	Satisfactory	Satisfactory

Note: SC mean non participant

Level 1, Leather - Chemical test

Laboratory CODE	pH	Chromic oxide Content %
L105	Satisfactory	SC
L106	SC	SC
L107	Satisfactory	Satisfactory
L108	Satisfactory	Satisfactory
L109	Satisfactory	SC
L110	Satisfactory	Satisfactory
L111	Satisfactory	Satisfactory
L112	Satisfactory	Satisfactory
L113	Sin calificación	SC
L114	Satisfactory	Satisfactory
L115	Satisfactory	Satisfactory
L116	Satisfactory	SC
L117	Questionable	Satisfactory
L118	Questionable	Satisfactory
L119	Sin calificación	SC
L121	Satisfactory	Questionable
L122	Satisfactory	SC
L123	Not satisfactory	SC
L124	Satisfactory	SC

Note: SC mean non participant

From the results obtained by the participants, the average coefficient of variation within the laboratory was calculated.

In-laboratory coefficient of variation

Physical and mechanical, test Level 1

	Tensile Strength N/mm^2	**Percentage Extension %**	**Tear Load N**
Assigned value x^*	23,69	62,36	186,09
Precision of the method s^*	1,04	4,82	11,15
Uncertainty u	0,31	1,42	3,38

Physical and mechanical, test Level 2

	Tensile Strength N/mm^2	**Percentage Extension %**	**Tear Load N**
Assigned value x^*	20,12	49,75	110,26
Precision of the method s^*	0,72	3,91	9,70
Uncertainty u	0,21	1,15	2,94

Finally there is the percentage of satisfaction that refers to the percent of laboratories considered as satisfactory in the method: % S = No. participants satisfactory / No. participants total x 100, with the following data:

	Leather Tensile Strength	**Leather Percentage Extension**	**Leather Teard Load**	**Leather pH**	**Leather Chromic Oxide %**
Leval 1	88,9	88,9	82,4	**81,3**	**90,0**
Level 2	72,2	83,3	100,0		
Average	**80,6**	**86,1**	**91,2**		

The metrological traceability is given in terms of the calibration of the measurement systems used by the participants themselves.

4. CONCLUSION

General conclusions

Physical tests: The results display consistency in evaluation. The method of resistance to tension is the one that presents the lowest percentage of satisfactory participants. The tear resistance method is the one with the highest percentage of successful participants.

Chemical tests: The lowest participation of laboratories is in the test of % of Chromium Oxide. The % of Chromium Oxide method is the one with the highest percentage of successful participants.

In relation to the 2015 Interlaboratory comparison of physical and chemical tests for leather tanned to the mineral proficiency test program, physical tests show an improvement in the average performance of the participants. In chemistry, no improvement is observed.

Conclusion: Recommendations

Questionable and unsatisfying participants are possibly not adhering correctly to the standard instructions of the method. Different results are a consequence of any of the following factors:

- Improper handling of the sample during the test.
- Conditions and operation of non-compliant measuring devices such as the following:

Physical tests:

- Damaged jaws
- Faulty test machines
- Cutting devices of specimens in poor condition

Chemical tests:

- Misaligned measuring instruments
- Poor reference materials

- Special cause errors due to lack of skill of operators.
- Calculation errors detected in some reports.

It is recommended that questionable and unsatisfactory participants carefully review the application of standardized methods and adhere to all the details indicated.

It is also recommended to promote among the participants the standardization of the method to improve the satisfaction percentage of the method.

5. ACKNOWLEDGEMENTS

The Author wishes to acknowledge the contribution to this Project of the following**:** José Julio Mares Hernández**;** José Rodolfo Tinajero Ramírez**;** Juan Enrique Iade Vergara**;** Patricia Rafaela Zeballos Trinidad and Carmine Le Rose Battafarono

6. REFERENCES

1) ISO 3376 IULTCS / IUP 6, *Leather - Physical and mechanical tests - Determination of tensile strength and percentage extension.* Third edition 2011-12-15.
2) ISO 3377-2 IULTCS / IUP 8, *Leather - Physical and mechanical tests - Determination of tear load - Part 2: Double edge loom.* First edition 2002-12-15.
3) ISO STANDARD 4045 IULTCS / IUC 11 *Leather - Chemical tests - Determination of pH.* Second edition 2008-02-15.
4) ISO 5398-1 IULTCS / IUC 8: 1, *Leather - Chemical determination of chromic oxide content – Part 1: Quantification by titration*. First edition 2007-08-01
5) ISO STANDARD 13528, Second edition 2015, *Statistical methods for use in proficiency testing by interlaboratory comparisons.*
6) ISO / IEC 17043 - 2010 *Conformity assessment - General requirements for proficiency testing*. First edition.