A Novel Preservation-cum-Unhairing Process for Sustainable Leather Manufacturing: An Unconventional Approach in Leather Making

J. Raghava Rao[1a], M. Sathish[2a], R. Aravindhan[2b] and P. Thanikaivelan[2c]

1a) Corresponding author: jrrao@clri.res.in, Inorganic and Physical Chemistry Laboratory, CSIR-CLRI, Chennai, India

2a) Co-author: leathersathish@gmail.com, Leather Process Technology Division, CSIR-CLRI, Chennai, India

2b) Co-author: aravindhanr78@gmail.com Leather Process Technology Division, CSIR-CLRI, Chennai, India

2c) Co-author: thanik8@gmail.com, Advanced Material Laboratory, CSIR-CLRI, Chennai, India

Abstract. Preservation (or) curing is an important unit process for transportation and storage of raw hides/skins without any deterioration. Popular preservation process is mostly achieved by reducing the moisture content of hides/skins using common salt (NaCl). Usage of salt in preservation process leads to generation of large amount of contaminated salt, total dissolved solids (TDS) and consume huge amount of water for subsequent rehydration step. On the other hand, lime-sodium sulphide based reductive process is commonly employed for the removal of hair from hides/skins. This process leads to generation of lime sludge and possible evolution of toxic hydrogen sulphide gas thereby making the working atmosphere more unpleasant. Several alternative techniques for preservation as well as unhairing process have been developed individually to replace salt and sulfide, respectively. However, a single compound performing dual functions such as preservation and unhairing action in neutral pH conditions has not explored so far. In the present work, a novel formulation has been developed, which possess the both preservation and unhairing potential, and applied on the hides/skins for storage up to 6 months at ambient conditions without dehydration. Low level of sulphide was used during alkaline fiber opening for removal of traces of hair. The strength and organoleptic properties are on par with salted skins/hides. The developed process completely eliminates the use of salt and 75% sulphide and also reduces the time and water required for soaking process. The developed system reduces 85% of pollution load discharged from soaking and unhairing processes.

1 Introduction

The hides/skins are susceptible for bacterial attack once flayed from animal. The normal time lapse between skinning and tanning process of green hides/skins demands for temporary preservation technique. Conventionally, salt (30-40% w/w) based preservation technique is widely practiced where the salt acts as dehydrant (Cooper & Galloway 1965). The conventional salt based dehydration technique demands for additional step such as rehydration in subsequent leather processing which consumes huge amount of water. Therefore, the conventional dehydration-rehydration model results in generation of a huge amount of wastewater with increased TDS load (Kannan et al. 2010). On the other hand, removal of TDS from wastewater requires sophisticated techniques like membrane filtration or reverse osmosis, which increase the cost of wastewater treatment process. This limitation can be capitalized by way of providing a suitable alternative for elimination of rehydration step in leather processing. Several attempts have been made to develop less salt and salt free preservation techniques to reduce the TDS load in wastewater (Money 1974; Bailey & Hopskins 1977; Bailey 1995). However, significant reduction in TDS has not been achieved. Polymeric compound based preservation technique has been developed using various molecular weight of polyethylene glycol (PEG). However, the cost of PEG is higher than the conventional salting technique (Kannan et al. 2010). Some attempts have been made to develop new preservation techniques which avoid the rehydration step (soaking) in leather manufacturing. Chandrababu et al. (2012a, 2012b, 2012c) provided a method for direct transportation of flayed hides/skins to tanneries by employing mobile chiller (4ºC), which eliminates the rehydration step, but the process is energy intensive.

Addition of ice to the raw stock would preserve the hides/skins (Hausam 1939) and this method is being followed on larger-scale in Switzerland, Germany and Austria, however, the process is applicable only for short duration. In order to increase the process efficiency, preservative containing ice has been employed in preservation process (Hausam 1951). But, the major limitation of the process is that draining of liquor containing high concentration of preservative. Short-term preservation can also be achieved by spraying bactericides and employing various plant extracts. Bailey & Hass (1988) and Bailey (1999) have provided an irradiation technique where gamma rays or electron beam applied on the hides/skins followed by packing in separate air tight bags for effective preservation. However, the process suffers from the requirement of skilled labor, high cost of investment and sophisticated instrumentation system.

Unhairing is a sequential process after soaking where the combination of lime and sodium sulfide is used conventionally as unhairing agents. But, the major limitations are generation of lime sludge and the possible release of toxic hydrogen sulfide gas during subsequent leather processing or from effluent treatment plant. Heidemann's Darmstadt process deals with spraying 10% sodium sulfide solution on the hair side of hides/skins and hung for 10-20 min. The degradation of epidermis layer enables easy removal of hair and the residual sulfide present in the skin matrix is further oxidized with 10% sodium peroxide solution (Heidemann 1993). Though the process is effective, the toxic sodium sulfide has not been replaced. Some attempt have been made to use hydrogen peroxide (Marmer 2004; Bronco et al. 2005; Morera et al. 2006), calcium peroxide (Gehring et al. 2003) and sodium percarbonate (Marmer & Dudley 2005) as sulfide free sharpening agents (oxidative unhairing), but it required higher quantity than sulfide, which in turn increases the process cost. Replacement of sulfide with thioglycolate (Frendrup 2000), sirolime (Cranston et al. 1986, 1986a) and dimethylamine (Somerville et al. 1963; Hetzel et al. 1965, 1966) is less effective and its odor makes the working atmosphere unpleasant. In acidic unhairing, concentrated acetic acid and salt is applied on the flesh side of fresh skins and stored overnight. Due to the combined actions of lyotropic effect induced by acetic acid and autolytic enzymes present in the skin matrix on basement membrane enables selective removal of epidermis from the grain surface (Heidemann 1993). Though the process eliminates the lime and sulfide, it is not suitable for dried and salted skins. Schlosser et al. (1985) utilized the lactobacillus culture, which selectively destroy the epidermis layer of the skin matrix thus enables the hair loosening. However, addition of salt is required to prevent acid swelling due to the formation of lactic acid during fermentation process, which increases the TDS load.

Several attempts have been made to use enzymes for the development of chemical free unhairing process (Green 1952; Bose 1955; Dhar 1974; Bradly et al. 1990; Feigel 1998), but the process cost is higher than the conventional lime/sulfide based system. Therefore, the development of a preservation technique without dehydrating the hides/skins matrix simultaneously enabling lime-free and low-sulfide unhairing process is essential in order to reduce the water consumption profile and pollution generation of pre-tanning process.

2 Materials and Methods

2.1 Preservation Efficiency of Salted and Preservation-Cum-Unhairing (PCU) Process

Raw sheep skins were procured from Permabur slaughter house, Chennai, Tamil Nadu, India and transported to CLRI pilot tannery within 2 h under cold condition and cut along the back bone. All the left halves were subjected to conventional salt based preservation and right halves were treated with developed PCU formulation. The preservation efficiency was monitored based on the hydroxyproline release from preserved skin. After the preservation period of 30 days, the salted skins were soaked, unhaired and chrome tanned as per the conventional process. The PCU processed skins were subjected to manual unhairing followed by lime based fiber opening and converted into wet-blue leather in a conventional way. The wet-blue leathers obtained from both salted and PCU process were converted into crust leathers.

2.2 Analysis of Physical Strength Characteristics and Organoleptic Properties

The physical properties such as tensile strength, % elongation at break (IUP 6 2000), tear strength (IUP 8 2000), grain crack load and distension at grain crack of crust leathers obtained from conventional and PCU processes were analyzed. The specimens for physical testing as mentioned above were obtained as per IULTCS standard method and conditioned for 24 h at 25±1°C and 65±2% RH (IUP 2 2000). The crust leathers were also evaluated for various organoleptic properties such as softness, grain smoothness, fullness, grain flatness and overall appearance by hand and visual examination. Each property was rated on a scale of 1-10, where higher point indicates better properties.

2.3 Analysis of Wastewater

Wastewater discharged from conventional and PCU based preservation system was subjected to COD, TS, TDS, TSS, TKN and Cl- analysis as per the standard method (Clesceri et al. 2005).

3 Results and Discussion

3.1 Preservation Efficiency of Salted and PCU Process

Preservation efficiency of the developed PCU process has been monitored over a period of 30 It is evident from Figure 1 that the hydroxyproline release increases with increasing time and reaches a maximum of 320 mg/kg for conventional process and 356 mg/kg for PCU process. It is clear that there is no significant increase in hydroxyproline for the PCU process over the salted technique. Therefore, it can be perceived that the preservation efficiency of the developed PCU process is on par with the conventional process.

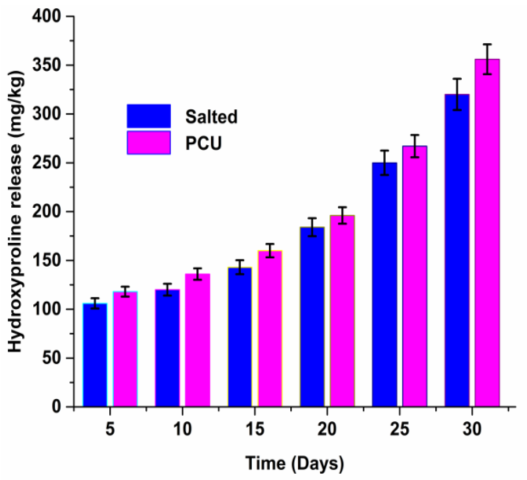

Figure 1. Effectiveness of the salted and PCU process against skin degradation

3.2 Analysis of Physical Strength Characteristics and Organoleptic Properties

The crust leathers obtained from conventional (salt) and experimental (PCU) processes have been subjected to various physical strength characteristics measurement and the results are given in Table 1. It has been observed from Table I that the physical strength characteristics of PCU treated leathers are on par with the conventionally processed leathers.

Table 1. Physical strength characteristics of crust leathers processed from salt and PCU processes

Characteristics	Salt	PCU
Tensile strength (N/mm2)	13.5±1	15.2±1
Elongation at break (%)	78.1±3	70.5±3
Tear strength (N)	26.5±4	25.1±3
Load at grain crack (kg)	16.6±1	19.4±1
Distension at grain crack (mm)	12.5±0.5	14±0.5

The organoleptic properties of crust leathers have been rated on a scale of 1-10. Higher points indicate better properties of final leather. The results indicate that the PCU leather exhibits better softness (9/10) and grain smoothness (9/10) than the conventionally processed leather (softness 8/10, smoothness 8/10). But, the fullness and grain flatness of conventional leather (8 /10) is slightly higher than PCU leather (7.5/10).

3.3 Analysis of Wastewater

The wastewater characteristics of soak liquor discharged from salt and PCU preservation system have been analyzed and the results are given in Table 2.

Table 2. Pollution/emission load from salted and PCU system

Pollution Parameters	**Emission Load (kg/ton)**	
	Salt Preservation	**PCU**
pH	7.2±0.2	6.9±.2
Cl-	123± 8	3±0.2
TS	268±14	41±4
TDS	235±20	36±2
TSS	34±3	6±0.4
TKN	3.7±0.4	2.7±0.1

It is evident from Table II that the pH of soak liquor from PCU and salted system is almost similar. Total solids discharged from conventional process is about 268 kg/ton, whereas for PCU system is only about 41 kg/ton. The other parameters like TDS/TSS have also been significantly reduced in PCU process due to the complete elimination of salt.

4 Conclusions

In this work, the preservation and unhairing process have been successfully interconnected through the development of preservation-cum-unhairing process. And the developed system reduces 85% of pollution load discharged from soaking process in addition to eliminating the lime and reducing the toxic sodium sulfide required for the hair removal process. Therefore, the developed preservation-cum-unhairing process would be a promising technology lead for sustainable leather manufacturing.

References

1. *Cooper, DR & Galloway, AC: 'Curing methods for wet salted hides. Part II. The reuse of salt for the curing of hides', Journal of American Leather Chemists Association, vol. 61, pp. 162–170, 1966.*
2. *Kannan, KC, Pradeep Kumar, M Rao, JR & Nair, BU: 'A Novel approach towards preservation of skin', Journal of American Leather Chemists Association, vol. 105, pp. 361-369, 2010.*
3. *Money, CA: 'Short term preservation of hides. II The use of zinc chloride or calcium hypochlorite as alternatives to sodium chlorite', Journal of American Leather Chemists Association, vol. 69, pp.112–120, 1974.*
4. *Bailey, DG & Hopskins, WJ: 'Cattle hide preservation with sodium sulfite and acetic acid', Journal of American Leather Chemists Association vol. 72, pp. 334–339, 1977.*
5. *Chandrababu, NK, Karthikeyan, R, Kumari, BS, Ramesh, R, Shanthi, C & Sadulla, S: 'A systematic study on the role of chilling temperatures on the curing efficacy of hides and skins', Journal of the American Leather Chemists Association, vol. 107, pp. 362-374, 2012.*
6. *Chandrababu, NK, Kumari, BS, Vimalarani, SH, Shanthi, C, Karuthapandian, S & Sadulla, S: 'Microbiological aspects of hide and skin preservation by chilling' Journal of the Society of Leather Technologists and Chemists, vol. 96, pp. 71-76, 2012.*
7. *Chandrababu, NK, Thiagu, R, Karthikeyan, R, Kumari, BS, Ramesh, R & Sadulla, S: 'Using a mobile chiller for hides: a green method to resolve the TDS problem' Journal of the Society of Leather Technologists and Chemists, vol. 96, pp. 200-209, 2012.*
8. *Hausam: 'Preservation by cooling', Journal of American Leather Chemists Association, vol. 36, pp. 44-48, 1939.*
9. *Hausam: 'Behaviour of hide during salting and the action on the hide protein', Journal of American leather Chemists Association, vol. 12, pp. 1-6, 1951.*
10. *Bailey, DG: 'Gamma radiation preservation on cattle hides: A new twist on an old story', Journal of American Leather Chemists Association, vol. 94, pp. 259–266, 1999.*
11. *Bailey, DG & Haas, MJ: 'Electron beam irradiation of fresh hides, salted hides and leather, Microbial control and effect of physical properties', Journal of American Leather Chemists Association, vol. 83, pp. 46–55, 1988.*