Zero Chrome Tanning Technology - An Approach for Ecofriendly Tanning

Victor John Sundar[1], Chellappa Muralidharan[1] and Asit Baran Mandal[2]

[1]Leather Process Technology Division,
Central Leather Research Institute, Adyar, Chennai-600 020, India. Phone: +91 44 24437230 Fax: +91 44 24911589 E-MAIL: johnsundar70@yahoo.co.uk
[1]Leather Process Technology Division,
Central Leather Research Institute, Adyar, Chennai-600 020, India. Phone: +91 44 24437230 Fax: +91 44 24911589 E-MAIL: cmurali62@yahoo.com
[2]Chemical Laboratory,
Central Leather Research Institute, Adyar, Chennai-600 020, India. Phone: +91 44 24915238 Fax: +91 44 24912150 E-MAIL: abmandal@hotmail.com

Abstract

Development of commercially viable zero chrome tanning technology has been an active area of research in recent years. With stringent norms being put to force, it has become necessary for researchers and tanning industry to focus their attention towards discharge of total dissolved solids, chlorides and chromium in the spent liquors of leather making. Chlorides and chromium discharges in effluents are the fundamental environmental concerns for leather processing. Several alternate approaches such as pickle liquor recycling, high exhaust chrome tanning and spent chrome liquor recycling are being employed. In this study an attempt has been made to eliminate salt usage and chrome discharge. The efficacy of this alternative system has been assessed by analyzing the spent liquors for TDS, chlorides and chrome content in leather. The physical and chemical properties of leathers processed through the alternate system skins were found comparable with conventionally tanned skins. The study indicates that the new tanning system is viable and can be adopted in large scale without any infrastructural changes. The study provides an economical and ecological solution to the long pending problem, which has been commercially implemented.

Keywords: Chlorides, Chromium, Ecology, Pollution, Salinity, Skins and hides, Tanning, Total dissolved solids.

1. Introduction

Conventionally 8 – 10% of salt on the weight of hide or skin is employed for the pickling operation. The salt let-out from the waste streams of pickling results in generation of Chlorides and Total dissolved solids (TDS) in the order of 80,000 to 100,000 ppm (Mwinyihija, et al. 2006). Extensive researches have been done on various methods of salt free pickling and chromium management (Morere, et al. 2007; Munz, et al 1997; Sundar, et al. 2002). The

economical and operational viability of the treatment system is not ensured because of high levels of salinity and high chromium levels in the effluents (Cassano, et al. 2001; Junior et al 2007; Kimbrough, et al. 1999; Sundar, et al. 2001; Sundar, et al 2011; Sreeram, et al. 2003). The cost associated with the treatment and the disposal of huge quantities of reject arising from the RO plants are also cause of concern. An approach has been made towards salt free zero chrome tanning technology which solves the problems associated with tanning. The technology completely eliminates pickling and basification steps through process modifications.

2. Material and Methods

Ten delimed goat skins (of weight ranging 1 – 2 Kg at wet salted stage) at pH 8.0 were cut into two halves with left half and right half taken for experiment and control respectively. Commercial grade basic chromium sulphate (BCS), sodium formate and Magnesium oxide were used for tanning studies. Shrinkage temperature and stratigraphic chrome distribution in wet-blue leathers were analysed by using SLTC official method of analysis.

2.1 Process details

The left half of the delimed pelts meant for experiment were treated with 0.2% *(w/w)* formic acid to attain pH 5.0-5.5. Then dry chrome tanning method was followed with addition of 3% BCS and 0.5% sodium formate and drummed for 1 hour followed by addition of 3% *(w/w)* BCS and 0.5% *(w/w)* sodium formate and further drumming for another hour. After ensuring complete penetration of chromium throughout the cross section of the pelt, the drum was fed with 100% water in which 1% sodium bicarbonate was dissolved in six instalments for 60 minutes. The pH of the leather was adjusted to 4.0 at the end of tanning. The right half delimed pelts were processed by conventional chrome tanning process using conventional pickling and tanning in 50% pickle bath using 8% basic chromium sulphate. The pH of the bath was adjusted to 4.0 after flooding with 50% water. The pH profile of both the experiment and control process liquors has been monitored continuously. Then the chrome tanned leathers were aged for twenty four hours and were assessed. Then the leathers were post tanned and assessed for their organoleptic properties.

2.2 Spent liquor analysis

The spent tan liquor was analysed for TDS, Chlorides and chrome content as per the American wastewater Association method (AWWA 1998).

2.3 Scanning Electron Microscopic (SEM) Analysis

Chrome tanned leather specimens were gold-coated using Edwards E306 sputter coater device and analysed using FEI, Quanta 200 Scanning Electron Microscope.

2.4 Strength property analysis

Strength characteristics of the crust leathers such as tensile strength and tongue tear strength were tested using an Instron tensile tester. Grain crack and grain burst test were carried out

using lastometer as per SATRA (1992). Leather samples for the physical testing were taken parallel to backbone of the leather samples following the official procedure for sampling and testing (IUP 1958).

2.5 Organoleptic functional property analysis

Chrome tanned leathers were subjected to organoleptic assessment for softness, fullness, grain smoothness, colour uniformity and general appearance by hand and visual examination. The leathers were rated based on a scale of 0 –10 grade points for each functional property by six experts.

3. Results and Discussion

3.1 Spent tan liquor analysis

The spent tan liquor analysis as shown in Table 1 indicates substantial reduction in TDS and chlorides due to elimination of conventional pickling operation. While chloride has been completely eliminated from the waste streams the reduction is more than 70% in the case of TDS. The reduction in TDS is due to elimination of sodium chloride as well as elimination of steep variations in pH. In conventional processing such pH variations lead to generation of significant quantities of neutral salts. Spent tan liquor analysis for chromium results 200±10 ppm and 2500±10 ppm for experimental and control processes respectively. Therefore, above 90% reduction in chromium content in the spent tan liquor is made possible due to use of this new salt-free zero chrome tanning process. Though it is known that chrome tanning at elevated pH lead to higher chromium uptake, often such methods lead to non – uniform distribution. The present method was not associated with such drawbacks, as shown in Table 2.

3.2 Shrinkage temperature and Stratiographic chromium distribution

The shrinkage temperature and the chrome content as %Cr_2O_3 (based on dry weight) of the chrome tanned leathers of experimental and control process are given in Table 2. The results indicate that 30% higher uptake of Cr_2O_3 has been obtained for the experimental leathers as compared to the control leathers and resulted in higher thermal stability.

3.3 Scanning Electron Microscopic (SEM) Analysis

Scanning electron micrographs of cross section of experiment as well as control chrome tanned leathers with magnification of x300 are shown in Figure 1 and 2 respectively. The results indicate that experimental leathers have more compact and uniform fibre structure as compared to that of control leathers.

3.4 Strength and Organoleptic functional property analysis

The organoleptic property analysis of the chrome tanned leathers are shown in Table 3. The

results indicate that experimental leathers have comparable organoleptic properties with conventionally processed leathers. The physical testing characteristics of the crust leathers are shown in Table 4. The results indicate that strength properties such as tensile, tear, grain crack are comparable for experimental and control leathers.

4. Conclusion

This study has overcome several emerging environmental issues and negative perceptions encountered in managing chlorides and TDS in tannery effluents. The elimination of salt usage and chrome discharge made in this study has led to highly convincing results. The functional and aesthetic properties of leathers processed through the salt free zero chrome tanning technology were found to be better and comparable to the conventionally tanned leathers. Thid technology can be taken to be a long lasting scientific solution thereby yielding huge economic benefits and is a viable option for sustenance of global tanning industry.

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TABLE 1

Spent tan liquor analysis

Process	**TDS (ppm)**	**Chromium as Cr_2O_3 (ppm)**	**Chloride as Cl^- (ppm)**
Experiment	8090±50	200±10	Nil*
Control	98830±50	2500±10	54400±10

*Traces carried over from preservation

TABLE 2

Analysis of chrome tanned leathers

	Experiment	**Control**
$\%Cr_2O_3$	4±0.5	3±0.5
Ts^oC	105±2	102±2

TABLE 3

Organoleptic properties of chrome tanned leathers

Property	Experiment	Control
Grain characteristics	8	7
Fullness / Handle	7	7
Colour uniformity	8	7
General appearance	7	7

(On Ten Point Scale: 0 – Poor; 10 – Excellent)
The values are mean value given by six expert

TABLE 4

Physical testing characteristics of crust leathers

Property	Experiment	Control
Tensile strength (Kg/cm^2)	230±5.0	215±5.0
% Elongation at break	64.0±3.0	62.0±3.0
Tongue tear strength (Kg/cm)	23.0±0.5	22.0±0.5
Grain crack strength (Kg)	>40	>40
Distension (mm)	14.0±0.4	12±0.4

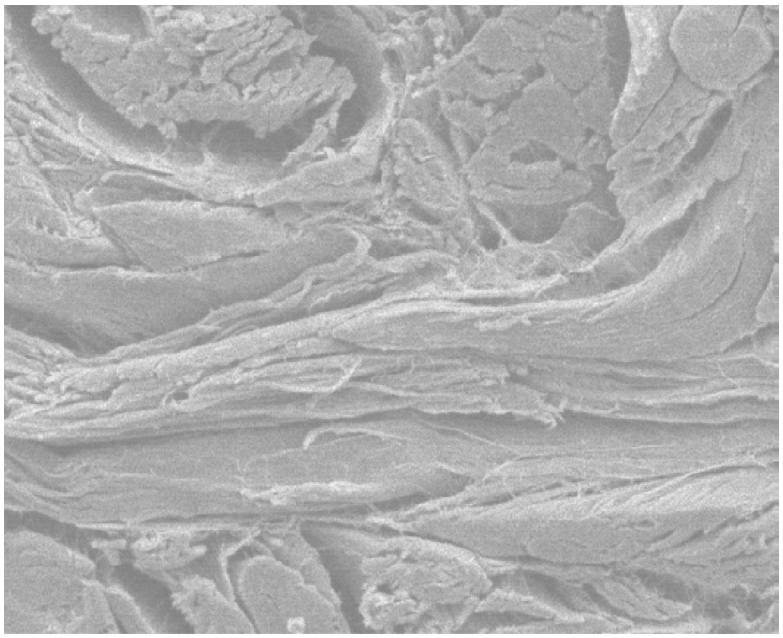

Figure 1. Salt free zero chrome tanned leather (x300)

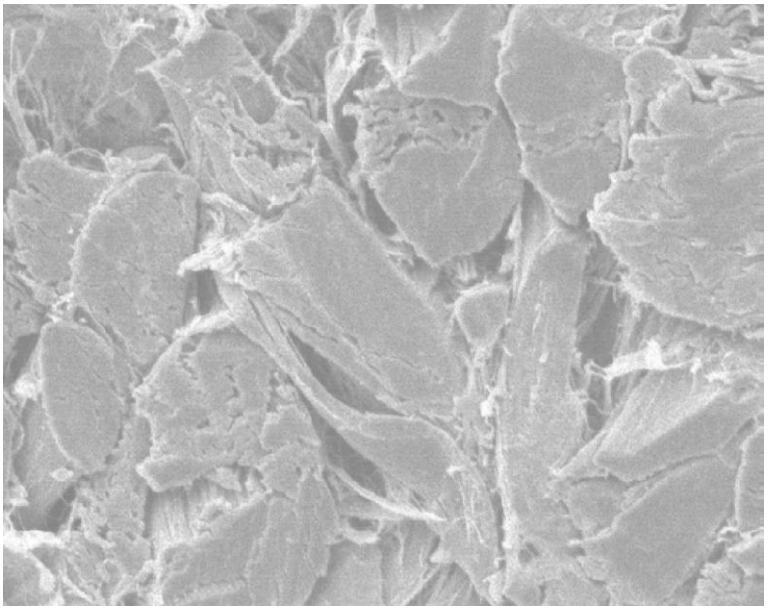

Figure 2. Conventional chrome tanned leather (x300)