Development of hair-save unhairing method using organic thio compounds in pre-tanning stages of leather production.

Ariful Hai Quadery[1], Md. Tushar Uddin[1], Md. Abul Kashem Azad[1], Murshid Jaman Chowdhury[1], Amal Kanti Deb[2], Md. Nazmul Hassan[3]

[1]Leather Research Institute, BCSIR, Nayarhat, Savar, Dhaka-1350, Bangladesh.

[2] Institute of Leather Engineering & Technology, University of Dhaka, 44-50 Hazaribugh, Dhaka-1209, Bangladesh.

[3] Department of Applied Chemistry & Chemical Engineering, University of Dhaka, Dhaka-1000, Bangladesh.

Abstract

The function of liming and unhairing is to remove hair, interfibrillary components, fatty matters and epidermis and to open up fiber structure. The process of unhairing depends upon the phenomenon of destroying or loosening and removal of hair by chemical and mechanical means. The keratinous material (hair, hair root, epidermis etc.) are eliminated from the pelts conventionally with the mixture of sulphides (Na_2S, NaHS) and lime which contribute to the high Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Dissolved Solid (TDS) etc. in the tannery effluent. The study showed that significant amount of reduction in pollution concerning parameters like COD, BOD, suspended solids, Nitrogen and Sulphide in tannery waste water due to use of thio compound as unhairing agent. This reduction is explained by the fact that thio compound is non toxic. The intact hair is also collected as new raw material for fertilizer rather than being discharged with the effluent. The strength and organoleptic properties, chromium content and SEM analysis of the leather processed using thio compound, indicates that the quality of leather is also considerably improved.

This paper is focused on development of eco-friendly hair saving unhairing method using organic thio compound as an unhairing agent and to reduce the use of lime and sulphide in liming operation. It also discusses about the quality of leather and discharged liming waste water and compare with the conventional liming.

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Keywords: Biological Oxygen Demand (BOD), Chemical oxygen demand (COD), Hair-save, Immunization of keratin, Liming, Scanning electron micrograph, Unhairing.

1 Introduction

THE leather processing involves various operations in a cascade manner form raw hide to crust leather. The complete leather manufacturing process is divided into three fundamental stages: beam house or pre-tanning, tanning and post tanning. The beam house stages comprise of soaking, liming, unhairing, deliming, bating and pickling.

Soaking [1], [2] is the first pre-tanning operation for treatment of hides and skins with water to clean and rehydrate as green condition. In this stage hides and skins are washed and soaked with surfactants and anti-microbial compounds before further processing.

The soaked hides and skins are treated with lime and sodium sulphide mixture which gives desired swelling of collagen structure to open up the fiber bundle. The quality of ultimate finished leather largely depends on this operation.

A common industrial practice of unhairing and liming is one step. Unhairing is the process of removing hair from the pelt without any damage to them. Once the hair shaft detached from the hide surface it is free to float in the bath and can be separated by filtration (hair saving) or chemically dissolved in the bath itself (destructive unhairing). The hair dissolution implies a much higher organic pollution of the waste water, whereas hair saving technologies needs a proper disposal of the recovered hair.

1.1 Sulphide unhairing and liming

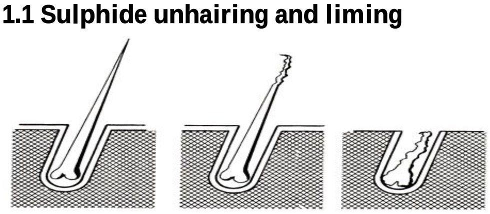

Fig. 1. Action of unhairing agent during Na_2S liming system

sodium sulfide and sodium sulphydrate used are sufficient

- *Ariful Hai Quadery, Leather Research Institute, BCSIR, Nayarhat, Savar, Dhaka-1350, Bangladesh, PH-01123456789. E-mail: quadery.lri@gmail.com*
- *Md. Nazmul Hassan, Department of Applied Chemistry and Chemical Engineering, University of Dhaka, Dhaka-1000, Bangladesh, PH-+8801714391916. E-mail: nazmulek@gmail.com*
- *Murshid Jaman Chowdhury, Leather Research Institute, BCSIR, Nayarhat, Savar, Dhaka-1350, Bangladesh, PH-+8801718333335. E-mail: jaman.bcsir@gmail.com*

to break down the –S-S- bonds that characterize the keratin structure of the hair [2]. In this process the skins are introduced into a drum or paddle and sodium sulfide, sulphydrate and lime are added. The destruction of the hair results rapidly and within (half an hour) the hair loses most of its fiber structure. The hair destruction system is quite common in leather process for all type of production.

In alkaline solution the keratin –S-S- bond may be broken according to the following equation [1], [5].

$$R\text{-}S\text{-}S\text{-}R + 2Na_2S = 2R\text{-}SNa + Na_2S_2$$

1.2 Hair saving unhairing

The hair saving process involves [6], [7] the introduction of enzymes with lime in a balanced system with careful attention to temperature and concentrations. Removal of hair takes place by hydrolysis of the soft proteins in the hair follicle. The thio-compounds have been used in various industrial applications. It has the capacity to cleavage [8] the cystine molecule of keratin protein.

Here the principle of liming by immunization [3], [9], [10] is generally been used. The soaked hides /skins are pretreated in the drum with an alkali like calcium hydrate. Under the influence of alkali the cystine of the hair transforms into lanthiamine, which can no longer hydrolyzed by reduction (immunization). The subsequent addition of sodium sulphide, for example causes a reduction only in unimmunized hair roots which leads to hair loosening. The comparatively well preserved hair can then be recovered by means of a screen [11], [12].

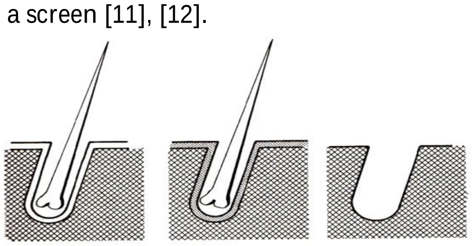

Fig. 2. Action of unhairing agent during a hair-saving system

1.3 The aim of this study

1. Application of organic thio compound as an unhairing agent to reduce the use of lime and sulphide in liming operation.
2. To evaluate the wet blue and leather quality.
3. To study the effect of discharge liming water comparison with conventional liming.

2 Materials and Methods

2.1 Raw hide

In the preliminary trials 8 pieces of raw cow hides (each approximately 2 Kgs) were taken and soaked conventionally. The concentration of thio organic compound was varied over the range of 0.5-2.0 with 1% lime in the liming operation. All the chemicals percentages were based on salt weight and are commercial grade except the organic thiol compound which was prepared from reagent grades chemicals. In this work (no of) domestic cow sides weight ranges 6-7 Kgs were selected as raw materials.

2.2 Shrinkage temperature analysis

The shrinkage temperature (Ts) of samples, which is a measure of hydrothermal stability of leather, was determined [13] using a Theis shrinkage meter. Each value reported is an average of three experiments.

2.3 Analysis of hide substance content of leather samples

Total nitrogen contents of leather samples were measured [13] according to GB4689 using BUCHI-339 device. Hide substance contents of leather samples were calculated by multiplying the measured total nitrogen contents of leather samples by 5.62.

2.4 Mechanical properties of crust leather samples

Mechanical properties such as tensile strength, elongation, tear strength and grain crack strength were measured [13] according to standard procedures. Each value reported was an average of four (2 along the backbone, 2 across the backbone) measurements.

2.5 Analysis of waste water

Waste water was collected from dehairing process for the testing of total solids (TS), chemical oxygen demand (COD) and biochemical oxygen demand (BOD) and sulphide by standard method [9]. The results reported were average values of three experiments for each sample.

2.6 Analysis of total nitrogen in waste water

Total nitrogen contents of waste water collected from dehairing process to deliming process was measured [9] according to standard method.

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2.7 Microscopic studies

Experimental as well as control leather surfaces were examined for variations in surface characteristics using FEI, Quanta 200 Scanning Electron Microscope [9], [14]. Samples from crust leather sides were directly cut into specimens with uniform thickness without any pretreatment.

2.8 Visual assessment

The experiment and control leathers were assessed for organoleptic properties by three experts.

3 Results and Discussion

Recipe 1: Conventional soak and lime process for wet salted hides (% based on wet salt weight.)

Process	%	Chemical	Temperature	Time in minutes	pH
Dirt soak	150	Water	28^{0}C	30-60	
Drain Soak	120 0.5 0.25 1.0	Water Sodium carbonate Non-ionic emulsifier Enzymatic soaking agent	28^{0}C	240-360	9.5-10.5
Drain Wash Drain	100	Water	26^{0}C	10	
Lime	100 1.0 1.0	Water Liming auxiliary Sodium hydrosulphide 72%	26^{0}C	45	
	1.0 1.0 0.2	Lime Sodium sulphide 62% Non-ionic emulsifier		60	
	50	water	26^{0}C		
	2.0	lime		30	
Run on automatic-stop 50 mins/run 10 mins for 12-14 hours					
Drain Wash Drain	100	water	26^{0}C	15	
Drain Wash Drain	100	water	26^{0}C	10	
Take out for fleshing					

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Recipe 2: Hair saving and lime process using organic thio compound for wet salted hide (%based on wet salt weight.)

Process	**%**	**Chemical**	**Temp.**	**Time in minutes**	**pH**
Dirt wash	**150**	**Water**	**28^{0}C**	**30-60**	
Drain Soak	 120 0.5 0.25 1.0	 Water Sodium carbonate Non-ionic emulsifier Enzymatic soaking agent	 28^{0}C	 240-360	 9.5-10.5
Drain Wash Drain	 100	 Water	 26^{0}C	 10	
Immunise	120 1.2 1.5	Water Thio organic compound lime	26^{0}C	 60	
Hair release	1.0 0.2	Sodium hydrosulphide 72% Non-ionic emulsifier		 20	
				20 stop 90 with screening of hair	
Lime	30 1.5 0.5	water lime Sodium sulphide 62%	26^{0}C	 30	
Run overnight for (Run 10 mins, stop 50 mins) for 12-14 hours					
Drain Wash	 100	 water	 26^{0}C	 10	
Drain Wash	 100	 water	 26^{0}C	 10	
Drain and take out for fleshing					

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Table 1: Unhairing at different dosage of thio compound

	Condition of limed pelt	
To be detected lime thio compound dosage (% on salted weight)	Unhairing degree	Scud
0.5	No loosening of hair	Present
1.0	Moderate loosening of hair	Present
1.5	Good loosening of hair	Presence is less
2.0	Excellent Loosening of hair	Clear pelt

Average value of two experiments

3.1 Preliminary unhairing

Preliminary unhairing experiments were performed on laboratory scale. Satisfactory unhairing occurred at 2% concentration. The result of unhairing trials are tabulated in table-1.

From the visual observation during unhairing it was quite comfortable to assess the extent of hair and scud removal.

Unhairing studies conducted at the pilot plant scale on three match sides that unhaired using thio compound (recipe 2.) were unhaired using thio compound with three corresponding matched hide sides for the control (recip 1.)

The processes were conducted by stainless steel laboratory drums rotating in temperature controlled bath.

The half sides were processed to wet blue and samples were collected for shrinkage temperature and determination of chrome content. The remaining half sides then tanned to crust leather and samples were collected for physical testing.

In recipe-1, 3.5% sodium sulphide and 4% lime are used. A solution of sodium sulphide alone with admixture with lime is a strong unhairing agent. It is reported that when lime alone is used, it requires longer time to cause hair removal. Unhairing effect of sodium sulphide is maximum when SH and OH ions in the solution are present equal quantities. It is also reported only 0.6%Na_2S is required for a hair burn process. In practice much higher amount of sodium sulphide are added. The main reason for this is the fact. The rate of unhairing is on the concentration of sulphide ions.

$$2Na_2S + 2\ H_2O = 2\ NaHS + 2\ NaOH$$

$$2NaSH + Ca\ (OH)_2 = 2NaOH + Ca(SH)_2$$

Here sodium sulphydrate act as an unhairing agent.

Total period in conventional liming was about 20-22 hours from the beginning. Next morning, drained away the liquor and run the drum 20 minutes for pulping out the hair. Then rinsed in water, unhaired and fleshed.

When the keratin protein in the hair cannot be chemically degraded and solubilized, it is said that hair is immunized and that such resistance results from the immunization phenomenon.

In recipe 2., the sodium hydrosulphide was used to replace the sodium sulphide partialy and this reduces the alkalinity available from the dissociation of sodium sulphide in water. Thio compound were used as reducing agent (HS-CH_2-CO_2-H).

The soaked hides were pretreated in the drum with a lime and thio compound. Under the influence of lime, the cystine of the hair transforms into lanthionine, which can no longer hydrolysed by reduction. In alkaline solution, the keratine –S-S- bond may be broken according to the following equation [4].

$$R\text{-}S\text{-}S\text{-}R + H_2O = R\text{-}SOH + R\text{-}SH$$

The subsequent addition of sodium sulphide causes reduction only unimmunized hair roots, which leads to hair loosening. Total 1.5% sodium sulphide was used in this experimental trial.

At pH 9.5-10.5, the thio compound spread as far as the root of the hair and started to hydrolyse the pre-keratin of the hair root. The pH value rose to 12.0-12.5 with the addition of lime and the reducing activity of thio compound consequently increases. Under the influence of lime the immunization of the hair shaft was observed within 90 minutes.

At this point, sodium sulphydrate was added which further reduced and hydrolysed the pre-keratin. The well preserved hair was recovered by screening.

In this work sulphide consumption was less in the developed process (recipe 2.) than the conventional recipe 1. The procedure can be carried out in a drum or paddle and also possible to collect hair.

3.1 Standardization of unhairing process

8 pcs of raw cow hide (each approximately 2 Kgs) were soaked. The concentration of thio organic compound was varied over the range of 0.5-2.0 with 1% lime. All the chemical percentages were based on soaked weight. The unhairing efficiency for each trial is given in table 1.

Table 2: Physical and chemical action on prepared wet blue

Test	Thio-compound unhairing	Sulphide unhairing
% Increase in weight	55	45
% Cr_2O_3	3.3	3.5
% Wrinkles	Less prominent	Prominent
Shrinkage Temperature	102^0C	100^0C

The hair-saving unhairing process was evaluated by measuring % weight change and the degree of wrinkling. The % Cr_2O_3 in the resulting wet blue leather was also determined as it is shown in the table 2. Both the shrinkage temperature and chrome content values are found considerably improved.

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Table 3: Physical-Mechanical properties of crust leather

Test	Thio compound unhairing	Sulfide unhairing
Tearing load (N)	172	165
Grain distention (mm)	7.6	8.3
Shrinkage temperature (^0C)	101	101
Tensile strength (N/mm^2)	24.32	22.43
Elongation (%)	35.52	39.51

Table 3 displays the physical tests, tear strength, tensile strength for both processed leather. The thio compound treated leather can be used for shoe upper since the value for tearing load and grain cracking was more than 120 N and 7.0 mm for distension.

The hair-saving unhairing process showed good physical-mechanical properties, comparable with those of the traditional. In fact the tear strength of the experimental leather was slightly higher as compared to corresponding control leather.

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Table 4: Technical properties of crust leather

Technical properties	Thio-compound unhairing	Sulphide unhairing
Roundness	5	5
Fullness	5	4
Softness	5	4

The unhairing quality was evaluated by the appearance of the hair root on the leather by the roundness and softness after being staked.

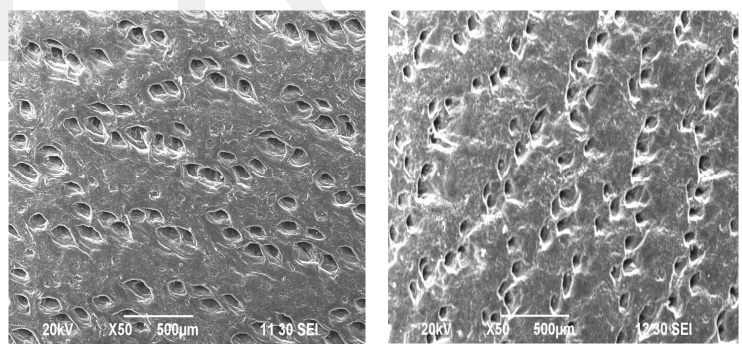
The assessment results of the technical properties of hair saving unhairing system incomparision with the traditional sulphide unhairing system are reported in Table 4. A conventional scale of grades ranging from 1 (worst performance) to 5(least performance) has been used. It may be observed that the crust leather obtained by hair saving unhairing system and traditional sulphide unhairing system show quite similar technical properties.

Table 5: Comparison between the Polluting charge of (unhairing Exhaust Bath of thio-compound and sulfide)

Test parameter	Hair saving (thio compound)	Hair pulping (sulphide unhairing)
COD mg O_2/l	22,700	47,900
BOD mg O_2/l	12000	31,000
N_{Tk} mg/l	1800	2560
TSS g/l	4.7	6.2
S^2 mg/l	447	771

The beam house phases, particularly the liming process, make up the most constituent part of total pollution produced due to their considerable contribution in the chemical and biochemical demand and total nitrogen and suspended solid.

Hair-save unhairing process has been applied that significantly reduce (25-30%) the BOD, COD and the total solids in the liming discharge. The result also shows the reduction of the sodium sulphide used with the consequent reduction of nitrogen. This is due to the presence of pollutants in low amounts of waste water in the case of developed hair-save unhairing system.



3(a) 3(b)

Figure: 3(a)- Scanning electron micrograph of a control and 3(b)- experimental crust leather showing the grain surface at magnification of X50

Scanning electron micrograph of crust leather samples processed through conventional unhairing and hair save unhairing process, showing the grain surface at a magnification of X50 are given in Fig. 3(a) and 3(b) respectively. It is seen that the hair pores of experimental samples appears to be much cleaner than control. This indicates that, hair save unhairing system able to perform unhairing without trace of hair. These observations are consistent with the conclusion mentioned above.

Conclusion

The possibility of unhairing using thio compound has been explored in this study. The use of thio compound has been found as excellent unhairing agent. The grain character and the strength properties of processed leather have been found to be good when composed to experimental leather. It is observed that hair was recovered easily by screening. This study was carried out in drum and the condition needs to modify for collection of hair. This brings about a significant reduction of the sodium sulphide and suspended solids with the consequent reduction in odour (H_2S gas).

The global concern for cleaner leather production has led tanneries to reduce the elimination of toxicity in their effluents. The possible application of hair saving unhairing process using thio compound confirmed.

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