Painting Unhairing for Manufacture of Upper Leather

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Abstract— **The unhairing step is a heavy pollution operation in the leather industry. The conventional lime-sulfide process produces a large amount of sulfide, which is toxic to health and difficult to dispose. Moreover, conventional process leads to the destruction of the hair causing increased chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total suspended solids (TSS) loads in the effluent. Painting unhairing process is hair-save process in which the soaked skins are piled to drain off surplus water and then painted on the flesh side with a "paint" which may be made from hydrated lime, water and sodium sulfide (fused). The sodium sulfide and lime dissolves in the water and penetrate through the corium and dissolve the keratin cells which enclose the hair roots. In the present study, an attempt has been made to produce upper leather using two methods of unhairing : painting unhairing (Experimental) and hair burning (Control). The strength characteristics of the experimental leathers are found to be comparable to those of control leathers. The organoleptic properties of the experimental leathers were shown to be similar or even better (especially softness) than the control leathers. The evaluation of softness shows that experimental leather has greater softness. The physical and chemical analysis indicates that the experimental leathers are comparable to control leathers in terms of all the properties. One of the main benefits of this work is the lower environmental impact. The spent tan liquor analysis shows significant reduction in sulfide loads compared to control.**

Index Terms— **Painting unhairing, Hair burning, Hair save, Sulfide reduction**

I. INTRODUCTION

Leather processing involves a series of unit operations (Fig 1), of which the process of unhairing is the first major step in leather making. The pelt has to be freed from the epidermis and hair, including the hair roots, and the keratinous material filling the hair follicles, before proceeding to the next step, the tanning [1]. During the unhairing process, large quantities of water and toxic chemicals such as sulfide are employed, generating huge amounts of effluent that must be treated, as well as solid wastes, that could be reused or better treated to avoid soil and water contaminations [2-4]. The unhairing step is a heavy pollution operation in the leather industry. The conventional lime-sulfide process produces a large amount of sulfide, which is toxic to health and difficult to dispose. Moreover, conventional process leads to the destruction of the hair causing increased chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total suspended solids (TSS) loads in the effluent [5]. Therefore, there is the necessity to implement cleaner technology, with the substitution of potentially hazardous reagents, for less aggressive products, and more easily treated in treatment plants. Enzymes are gaining much importance on hair removal process, eliminating the necessity of using sodium sulfide. Enzymes can be used in all stages of leather manufacture, except, perhaps, the current process of tanning [6]. Alkaline proteases produced by bacterium found numerous applications in various industrial sectors. In the leather industry, the enzymatic treatment destroys undesirable pigments, increases the area of hide and produces cleanest hides. Alkaline proteases increase the speed of unhairing because the alkaline conditions allow the swelling of the hair roots, and the subsequent attack of protease on the hair follicle protein, enabling easy removal of the hairs [7].

Another alternative to the use of lime and sodium sulfide is the use of oxidizing agents for the unhairing of the hide. The application of oxidative hair removal with recovery of hair contributes for the replacement of sodium sulfide and the reduction of pollutants load in wastewater. Recently, more attention is being given to oxidative unhairing with hydrogen peroxide (H_2O_2) due to the fact that it can remarkably reduce the environmental impact [8]. Both the sodium sulfide and hydrogen peroxide act in highly alkaline conditions: however, the sodium sulfide acts as reducing agent while hydrogen peroxide acts as oxidant one, decomposing and transforming into water, thus generating wastewater less pollutant [9]. The other depilation method used very much on sheepskins is the painting of the flesh side with a "lime paint" a mixture of slaked lime and sodium sulfide solution. The - (OH)-and - (SH) - ions penetrate the skin from the flesh side until it reaches the epidermal tissues, which they destroy, thus leaving the wool loose. The pelts are not sufficiently limed by the painting; the fibres are not properly swollen or the fibrils adequately separated, so the pelts must be immersed in a lime liquor in order to obtain the other liming effects. The advantages of this process are firstly that the hair can be recovered and sold. Secondly, the process can act as a pre-liming and gradual plumping process, thus avoiding distortion of the fibre structure and giving a smoother grained leather. Thirdly, the restriction of the paint to the back of the skin reduces the amount of plumping and alkaline hydrolysis of the flanks. The disadvantages are the extra cost involved and the extra floor space required [10].

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The hair structure consists of the hair bulb in which the soluble proteins of the hair are picked up into the hair root; the shaft of the hair, of relatively constant diameter, in which the hair has formed an inert, cross-linked keratin protein; the tip, at which the diameter of the hair tapers down to a vanishing point. The action of chemicals on the hair is quite different in the three areas. During a hair saving system the epidermis and soft keratins in the hair follicle are slowly dissolved and the hair is removed by the root, leaving a clean follicle. During the hair burning system the chemical action is strong enough to destroy the hair. The tip of the hair, having the greatest exposed surface, is destroyed first with the rest following. Softened hair shafts remain in the hair follicle [11]. The loosening of the hair is due the chemical action of the lime liquor on the hair root or base of the hair shaft, whereby it is weakened and finally disintegrates. This weakening of the hair is dependent on the break down of the disulfide link of the amino acid, cystine (Fig. 2), which is characteristic of the keratin class of proteins, for example, wool and hair [12]. The aim of this research is to produce upper leather from goat skin using painting unhairing method and compare with conventional hair burning method.

II. MATERIALS AND METHODS

Materials

Wet salted goat skins were used for experimental and control trials studies. Chemicals used for pretanning, tanning and post tanning were of commercial grade. Chemicals used for the analysis of spent liquor were analytical grade reagents. In unhairing of small skins, particularly those with large quantities of hair such as sheepskins and many goatskins, the painting system is use. The painting is conducted with a solution of lime and sodium sulfide,, sodium sulfide alone , or sodium sulfide plus caustic soda. The strong reducing agent is painted on the flesh side of the skin and skins are piled in such a manner that the sulfide paint is sealed in. Care should be taken so that the hair does not come in direct contact with the strong sulfide painting solution. The skins are piled in a cool place, or hung over sticks, or folded along the backbone, generally overnight. Next day the skins are ready for pulling. In pulling the hair, the skin is laid over a beam with the hair side up, and the hair puller removes the hair by hand. The unhaired skin is then placed in an additional liming solution without sharpeners, usually overnight, and this is followed by deliming, bating and pickling.

Experimental and Control trials

Wet salted goatskins of uniform size and weight were divided into two sides from the back bone. Left sides unhaired by painting unhairing method and processed into wet blue leathers as experimental trial (Table I). Right sides unhaired by conventional hair burning method and processed into wet blue leathers as control trial (Table II). Both experimental and control leathers were processed into upper crusts following the process mentioned in Table III.

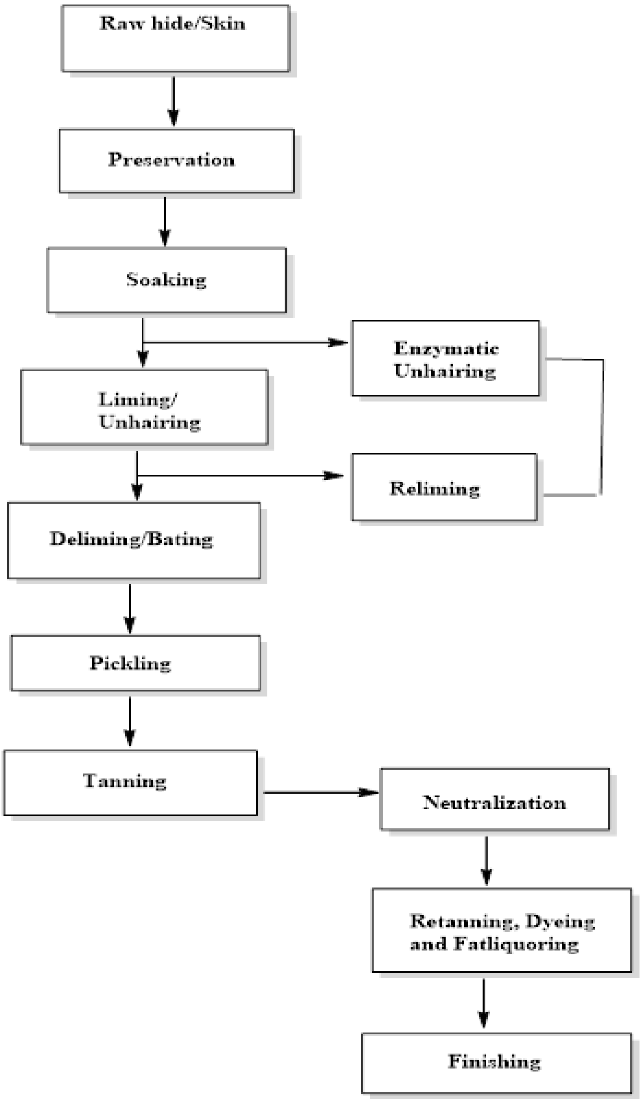

Figure 1. Various unit operations in leather processing

Measurement of Hydrothermal Stability of Leathers

The shrinkage temperature of control and experimental leathers was determined using Theis shrinkage tester [13]. Piece of tanned leather, cut from the official sampling position was clamped between the jaws of the clamp and immersed in solution containing 3:1 glycerol:water mixture. The solution was continuously stirred using mechanical stirrer attached to the shrinkage tester. The temperature of the solution was gradually increased and the temperature at which the sample shrinks was measured as the shrinkage temperature of the leathers.

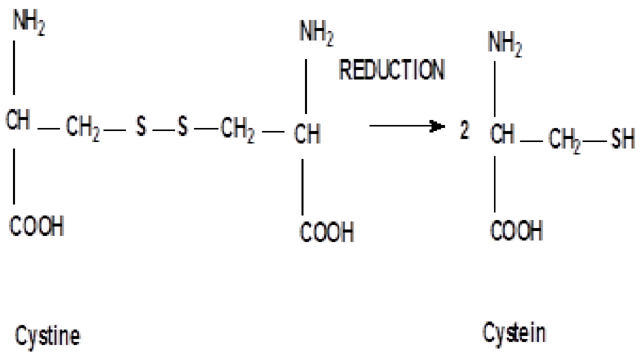

Figure 2. Break down of the disulfide link

Scanning Electron Microscopic Analysis of Unhaired pelt Samples

Samples from experimental and control unhaired pelts were cut from official sampling position. Samples were directly cut into specimens with uniform thickness without any pretreatment. Scanning electron microscope was used for the analysis. The micrographs for cross section were obtained by operating the SEM.

Visual Assessment of the Crust Leather

Experimental and control crust leathers were 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 points indicate better property.

Physical Testing

Samples for various physical tests from experimental and control crust leathers were obtained as per IULTCS methods [14]. Specimens were conditioned at 20 ± 2 °C and 65 ± 2 % R.H over a period of 48 hrs. Physical properties such as tensile strength, percentage elongation at break, [15] grain crack strength [16] and tear strength [17] were measured as per standard procedures. Each value reported is an average of four (2 along the backbone, 2 across the back bone) samples.

Analysis of Spent Liquor

The spent liquor from control and experimental trials were collected, filtered and analyzed for chemical oxygen demand (COD), Biochemical oxygen demand (BOD_5), and Sulfide as per standard procedures [18].

Table I
Painting Unhairing Method Formulation for Upper Leather Manufacture from Goat skins (Experimental)

Process	%	Product	Duration (min)	Remarks
Soaking	200	Water		
Painting	10	Water		
	2	Sodium sulfide		
	5	Lime		Apply the paste uniformly on to the flesh side and pile it over night. Next day unhairing
Reliming	100	Water		
	10	Lime		Dip the unhaired skins in this lime liquor for 2 days and then fleshing
Deliming	100	Water		
	1.5	Ammonium Sulphate	45'	pH 8-8.5 Check with indicator phenolphthalein, gave colorless
Bating	1	Bating Agent (Oropon)	60'	Temp 36-38°C
Pickling	100	Water		
	10	Salt	10'	
	0.2	Formic Acid		
	1	Sulphuric Acid	3x15' +40'	pH 2.8-3 drain 50% liquor
Tanning	50	water		
	8	Basic Chromium Sulphate	90	
Basification	0.5	Sodium formate		
	0.5	Sodium bicarbonate	3x15' +45'	pH 4. After piling for 48 hours, sam set and shave the leathers to a desired thickness (**1.2 mm**). Subsequently, post tanning was carried out.

Table II
Hair burning Unhairing Method Formulation for Upper Leather Manufacture from Goat skins (Control)

Process	%	Product	Duration	Remarks
Soaking	200	Water		
Liming and unhairing	10	Water		
	2	Sodium sulfide		
	5	Lime	4 hours	pH 12-13
Deliming and Bating	100	Water		
	1.5	Ammonium Sulphate		
	1	Bating Agent (Oropon)	2 hours	pH 8-8.5 Check with indicator phenolphthalein , gave colorless
Washing	200	Water	15 min	
Pickling	100	Water		
	10	Salt	10'	
	0.2	Formic Acid		
	1	Sulphuric Acid	3x15' +40'	pH 2.8-3 drain 50% liquor
Tanning	50	water		
	8	Basic Chromium Sulphate	90	
Basification	0.5	Sodium formate		
	0.5	Sodium bicarbonate	3x15' +45'	pH 4. After piling for 48 hours, sam set and shave the leathers to a desired thickness (1.2 mm). Subsequently, post tanning was carried out.

Chemical Analysis of Leathers

The chemical analysis was carried out for control and experimental leathers according to the standard procedures [19] for total ash content, % moisture, % oils and fats, % water soluble, % hide substance, % insoluble ash and degree of tannage. Triplicates were carried out for each sample and the average values are reported.

Table III
Formulation of Post-tanning Process for Making Upper Crust Leathers

Process	%	Product	Duration (min)	Remarks
Washing	200	Water	10	
Neutralization	0.75	Sodium bicarbonate	3X15	pH 5-5.5
Retanning	100	Water		
	8	Syntan	90	
Fatliquoring	9	Synthetic fatliquor	40	
Dyeing	3	Acid dye brown	30	
Fixing	1	Formic acid	3X10+30	pH 3.5

III. RESULTS AND DISCUSSION

Unhairing is the process of removing the hair from the pelt. It is traditionally one of the dirtier aspects of leather processing, from the point of view of the odour created (typically from the sulfide employed and the decomposed protein) and the polluting load generated. The traditional method of dissolving the hair is called 'hair burning.

Tanning trials for production of upper leathers were carried out on the goat skins that unhaired by painting method (experimental) and conventional hair burning method (control). The shrinkage temperature for both experimental and control upper leather is given in Table IV. From the table it is seen that both the experiment and control trials resulted in leathers with good shrinkage temperature.

Ecological Impact - Unhairing Effluents Analysis

The unhairing liquor contains highly organic matter in both control and experimental process liquor and it contributes to extremely high COD, BOD_5 and sulfide. Hence, it is vital to assess the environmental impact from control and experimental trials. The COD, BOD_5, and sulfide of the unhairing liquor for experimental and control trials have been determined and are given in Table V. From the table, it is observed that the COD, BOD_5 and sulfide of the unhairing liquor for the experimental trials are lower than the unhairing liquor from control trials.

Table IV
Shrinkage Temperature of Crust Leathers for Experimental and Control

Experiment	Shrinkage temperature, Ts (°C)
Painting unhairing (Experimental)	108±1
Hair burning (Control)	109±2

Scanning Electron Microscopy (SEM) Anaylsis

Scanning electron micrographs of unhaired pels samples, showing the cross-section at a in Fig. 3. The sample which had been unhaired using burning method-control (**a**), displays good opening of fibre bundles. The sample, which was painting unhaired-experimental (**b**), exhibits a slightly lower extent of opening up.

Tactile Properties of Crust Leathers for Experimental and Control

The organoleptic properties (visual assessment) of upper crust leathers for experimental and control are given in Fig. 4. (Higher numbers indicate superior properties). From the figure, it is observed that crust leathers processed by experimental (painting unhairing) and control (burning unhairing) tanning trials exhibited good softness, fullness, smoothness, general appearance and dye uniformity. Painting unhairing gave a smoother grained leather.

Strength Characteristics of Experimental and Control Crust Leathers

The physical strength measurements of experimental and control leathers are given in Table VI. The physical strength measurements viz., tensile strength, tear strength, Elongation at break, Load at grain crack and Distention at grain crack were found to be better for experimental leathers.

Table V
Characteristics of Unhairing Liquor for Experimental and Control

Experiment	COD (mg/l)	BOD_5 (mg/l)	Sulfide (mg/l)
Painting unhairing (Experimental)	18000 ±300	6000±250	4.5±0.5
Hair burning (Control)	27500±250	11000±250	350±5

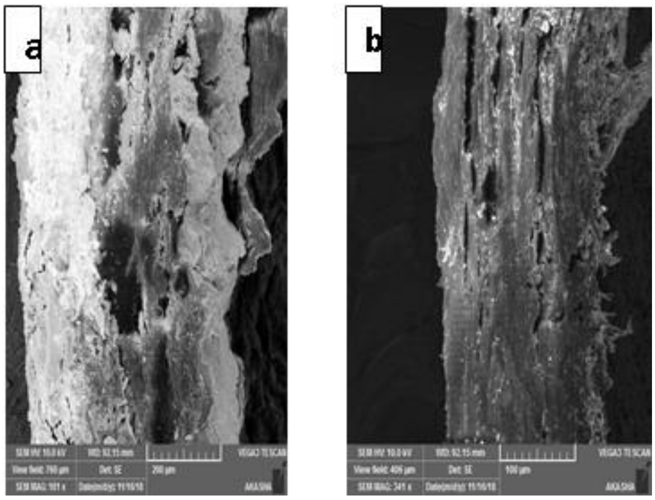

Figure 3. Scanning electron micrographs cross sectional view of unhaired pelt from (a) control (burning unhairing), (b) Experimental (Painting unhairing)

Figure 4. Graphical Representation of Organoleptic Properties of the Experimental and Control Leather

Chemical Analysis of the Crust Leather

The chemical analysis values of experimental crust leathers (Painting Unhairing) and control leathers (Burning unhairing) are given in Table VII. The chemical analysis data for the experimental leathers is comparable to that of control leathers.

Table VI
Physical Strength Characteristics of Experimental and Control crust Leathers

Parameter	Painting Unhairing	Burning Unhairing
Tensile strength (Kg/cm^2)	254±2	235±2
Elongation at break (%)	58±1.5	56±0.5
Tear strength (Kg/cm)	66±1.5	55±1.5
Load at grain crack (kg)	28±0.4	26±0.4
Distention at grain crack (mm)	12±0.3	11±0.3

Table VII
Chemical Analysis of experimental and control crust leathers

Parameter	Painting Unhairing	Burning unhairing
Moisture %	13.7	14.3
Total ash content %	2.25	2.3
Fats and oils %	2.45	2.6
Water soluble matter %	3.1	3.65
Hide substance %	52	51
Insoluble ash %	1.35	1.5
Degree of tannage %	52.7	52.84

IV. CONCLUSIONS

Painting is a traditional hair-save method for hair-sheep and goat skins; also, it is obligatory where the hair/wool is valuable. The skins are painted on the flesh side with a paste consisting of sodium sulfide, lime and water. After painting, the skins are stacked in a pile, hair side against hair side. The unhairing chemicals penetrate the skin from the flesh side and destroy the hair roots. In the present study, an attempt has been made to produce upper leather using two methods of unhairing: painting unhairing (Experimental) and hair burning (Control). The strength characteristics of the experimental leathers are found to be comparable to those of control leathers. The organoleptic properties of the experimental leathers were shown to be similar or even better (especially softness) than the control leathers. The evaluation of softness shows that experimental leather has greater softness. The physical and chemical analysis indicates that the experimental leathers are comparable to control leathers in terms of all the properties. One of the main benefits of this work is the lower environmental impact. The spent tan liquor analysis shows significant reduction in sulfide loads compared to control.

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