PERFORMANCE AND ECO-IMPACT OF REVERSE PROCESSED HAIR SHEEP GLOVING LEATHER*

by

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ABSTRACT

Leather processing, the world over, follows the pretanning, tanning, post-tanning and finishing sequence. It involves many process steps and huge pH variations thus discharges enormous amount of pollutants. A prudent analysis of the conventional leather process shows that the sequence follows 'do–undo' logic. In this study, the conventional processing sequence has been reversed to reduce the number of process steps and pH variations thereby achieving resource and pollution reductions. Hair sheepskins have been processed using both conventional and reverse processes for gloving application. Reverse process involves pretanning, post tanning, tanning and finishing sequence. The pH and charges of skin matrix after deliming are wisely utilized to apply post-tanning chemicals followed by chrome tanning salt. The processed leathers have been analyzed for chromium content, shrinkage temperature, strength and bulk properties. A set of turn-key tests have been carried out to verify whether the reverse processed leathers meet military specifications. The performance of reverse processed glove leathers is shown to be on par with conventionally processed leathers and meet the specifications predominantly. Especially, chrome content of reverse processed leathers is higher than control leather, which is corroborated through X-ray fluorescence analysis. The process enjoys significant reduction in COD and TS loads by 53 and 70%. Also, the process benefits from significant reductions in water, wastewater discharge, chemicals, time, power and cost compared to conventional process.

RESUMEN

Universalmente la curtición del cuero sigue la secuencia precurtido, curtido, recurtido y terminado. Esto involucra múltiples pasos y enormes oscilaciones del pH lo que ocasiona enormes descargas contaminantes. Un análisis a conciencia del proceso convencional de curtición demuestra que la secuencia sigue una lógica de "hacer-deshacer". En este estudio, la secuencia del proceso ha sido reversada para reducir el número de pasos y oscilaciones del pH y así lograr reducción en uso de recursos y contaminación. Pieles con pelo ovinas han sido procesadas por medio de los procesos convencional y el reversado para guantería. El proceso reversado involucra la secuencia de precurtido, recurtido, curtido y terminado. El pH ylas cargas de la matriz en la piel luego del desencale son sabiamente utilizadas para aplicar los productos del recurtido y en seguida se aplica la sal curtiente de cromo. Los cueros así procesados han sido analizados en cuanto contenido de cromo, resistencias, y propiedades extensivas. Una serie de pruebas claves se efectuaron para verificar si el cuero procesado en reversa cumple las especificaciones para uso militar. El comportamiento del cuero para guantes procesado en reversa se ha demostrado ser comparable al del proceso normal y cumple las especificaciones predominantemente. En especial, el cuero procesado en reversa contiene más cromo que el control, lo cual se corroboró por medio de análisis por fluorescencia de rayos x. El proceso goza de significante reducción del DQO y carga de ST [sólidos totales] por 53 y 70% [respectivamente]. A la vez, el proceso se beneficia por considerable reducción en agua, descarga liquida, productos químicos, tiempo, energía eléctrica y costos cuando se compara con el proceso convencional.

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INTRODUCTION

Conventional method of leather processing employs huge amounts of chemicals and other resources like water and power. This is mainly due to the traditional process logic followed, which involves many steps.[1,2] Further, it has been reported that the bulk properties of leather is affected by repeated acid and alkali treatments followed in conventional process.[3] These steps demand the use of acids and alkalis, which results in the generation of neutral salts. This results in a net increase of TDS, chlorides, sulfates and other minerals in tannery wastewaters apart from excessive usage of resources.[4,5] Pretanning, tanning, post tanning and finishing form four pillars of leather making.[6,7] Several attempts have been made to reduce or prevent pollution at source through in-process control measures.[8-12] This has gained importance in global leather industry. However, these improvements are specific to a unit operation. Implementation of all the advanced technologies and use of eco-friendly chemicals involve significant financial input and machinery requirements as well. This calls for the development of integrated cleaner leather processing methods for pollution reduction.

Attempts have been made to integrate the whole or part of leather processing steps.[13,14] Recently, integrated one-step wet finishing and one-step tanning and post tanning processes have been developed.[15,16] Reversing the conventional leather processing sequence for making upper leathers from goatskins and cowhides have been attempted.[17-19] Reverse leather process uses the pH condition of the delimed/degreased pelt, which is 7.5-8.0, for the application of post tanning chemicals. This is because the pelt is partially anionic in nature and the post tanning chemicals are also anionic. The detailed mechanism of the process has been reported elsewhere.[18]

This study aims at analyzing the performance and eco-impact of military glove leathers from hair sheepskins using reversed leather process sequence. The pollution parameters such as COD and TS loads have been quantified and analyzed. The performance of the final leathers has been evaluated in terms of physical as well as organoleptic properties. The chemical and physical properties of glove leathers from control and reversed processes have been analyzed for military requirements. Scanning electron microscopic analysis of processed leathers has been carried out. Techno-economic viability of the developed process has also been discussed.

EXPERIMENTAL METHODS

Materials

Wet salted hair sheepskins were chosen as the raw material. The chemicals employed for leather processing were of commercial grade. The laboratory grade chemicals used for analytical techniques were procured from S.D. Fine Chem Ltd., India.

Process Details

Twenty wet salted hair sheepskins were taken and soaked with three changes of 300% water, each with 3 h duration. The wet weight after soaking was noted. Liming was performed by using 2% sodium sulfide, 6% lime and 10% water (percentages based on soaked weight) adopting paint method of liming. Next day, the skins were manually dehaired using beam and blunt knife. Subsequently, the skins were relimed for three days using 4% lime and 200% water in a pit (percentages based on weight/soaked weight). Then the pelts were fleshed, scudded, and the weight of the pelts was noted. The pelts were washed with 200% water for 10 minutes. Subsequently, the pelts were delimed by treating with 100% water and 1.2% ammonium chloride (w/w) for 90 minutes. Completion of deliming was ascertained by checking the cross section of the delimed pelt for colorlessness to phenolphthalein indicator. The delimed pelts were washed with 200% water for 10 minutes. Then the pelts were degreased using 1% Degreasol WBI (Clariant Ltd.) for 45 minutes drumming without any float. The degreased pelts were washed with 200% water for 10 minutes. Degreased pelts were taken for conventional and reversed leather processes subsequently. A schematic representation for the comparison of process steps of conventional and reversed leather process is shown in Figure 1.

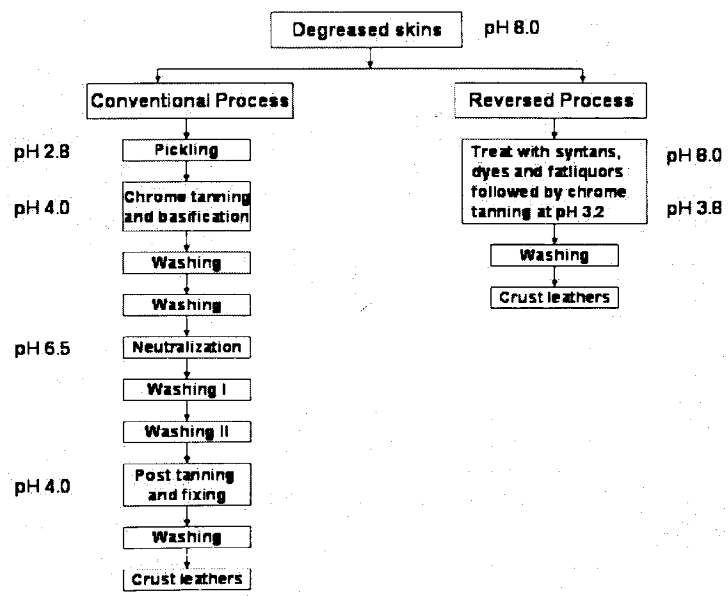

Figure 1: Schematic representation of conventional Vs reversed process

Process Details of Conventional Process (C)

Ten delimed and degreased hair sheepskins were used for the manufacture of the military glove leather through conventional process sequence in a stainless steel perplex drum with the size of 800 x 400 mm and agitation of 10 rpm.

Process/chemicals	%	Duration	Remarks
			% based on fleshed pelt weight
ickling			
Vater	100		
odium chloride	10	10 min	
ulfuric acid	1.2	3 × 10	The pH of the cross section of the pelt was found
Vater for dilution	20	min + 1 h	to be 2.8. 50% bath was drained.
hrome tanning			
asic chromium sulfate	8	2 h	
elugan GT-50 (BASF Ltd.)	0.1	30 min	
Vater	50	30 min	
ptimalin UPN/C (Munzing Chemie GmbH)	0.2	30 min	
odium formate	1		
odium bicarbonate	1	3 × 10	The pH of the cross section of the tanned leather
Vater for dilution	10	min + 2 h	was found to be 3.8. Bath was drained.
Vashing			
Vater	200	10 min	Bath was drained.

he leathers were piled for 24 h. The leathers were then sammed and shaved to a uniform thickness (0.6±0.1mm). The weight of e leathers was noted and termed as shaved weight. Rechroming was not done. Percentages of the following chemicals were based n shaved weight.

ost-tanning			
Vashing			
Vater	200	10 min	Bath was drained.
eutralization			
Vater	100		
odium formate	1		
mmonium bicarbonate	1.5	3 × 10	
Vater for dilution	10	min + 2 h	pH was found to be 6.3±0.1
eopristol SWF (Schill & Seilacher)	3	45 min	Bath was drained
Vashing I			
Vater	200	10 min	Bath was drained.
Vashing II			
Vater	200	10 min	Bath was drained.
etanning, dyeing and fatliquoring			
Vater	50		
ernol liquor SL (Clariant Ltd.)	3	30 min	
ernatan R7 (Clariant Ltd.)	3	30 min	
asyntan AN (BASF Ltd.)	3	45 min	
ptimalin FB (Munzing Chemie GmbH)	3	20 min	
ernol liquor SL (Clariant Ltd.)	3	20 min	Fatliquor was emulsified using 10% hot water at 60°C
oloderm black 2 PL (Colourtex)	3	30 min	Complete penetration of dye was checked.
ernol liquor ASN (Clariant Ltd.)	3	20 min	Fatliquor was emulsified using 10% hot water at 60°C
ptimalin FB (Munzing Chemie GmbH)	3	30 min	Fatliquor was emulsified using 10% hot water at 60°C
yncurol SLE (Munzing Chemie GmbH)	6	60 min	Fatliquor was emulsified using 10% hot water at 60°C
ixing			
ormic acid	2	3 × 10	
Vater for dilution	10	min + 1 h	Bath was drained.
Vashing			
Vater	200	10 min	Bath was drained.

eathers were hooked for drying. The dried leathers were conditioned, staked, trimmed and milled for 3 h.

Reversed Leather Process (E)

Ten delimed and degreased hair sheepskins were used for the manufacture of the military glove leather through reversed leather process sequence in a stainless steel perplex drum with the size of 800 x 400 mm and agitation of 10 rpm. Post tanning chemicals were applied on degreased hair sheepskins. The percentage offer of post tanning chemicals was designed by taking the account of pelt to shaved weight ratio. After the penetration of post tanning chemicals, pH of the pelt was adjusted to 3.2. At this stage, the tanning was performed using basic chromium sulfate. The final pH of leather was adjusted to 3.8 using sodium bicarbonate.

Process/chemicals	%	Duration	Remarks
			% based on flesh pelt weight
Water	50		
Neopristol SWF (Schill & Seilacher)	2	30 min	Fatliquor was emulsified using 10% hot water at 60°C.
Basyntan AN (BASF Ltd.)	1	30 min	
Optimalin FB (Munzing Chemie GmbH)	1	20 min	Fatliquor was emulsified using 10% hot water at 60°C.
Vernatan R7 (Clariant Ltd.)	1	45 min	
Vernol liquor SL (Clariant Ltd.)	2	60 min	Fatliquor was emulsified using 10% hot water at 60°C.
Coloderm black 2 PL (Colourtex)	1	20 min	Complete penetration of dye was checked.
Optimalin FB (Munzing Chemie GmbH)	1	20 min	Fatliquor was emulsified using 10% hot water at 60°C.
Syncurol SLE (Munzing Chemie GmbH)	2	60 min	Fatliquor was emulsified using 10% hot water at 60°C.
Formic acid	1	3 x 10 +	The pH of the cross section
Water for dilution	10	30 min	of the matrix was found to be 3.2.
Basic chromium sulfate	8	2 h	
Relugan GT-50 (BASF Ltd.)	0.1	30 min	
Optimalin UPN/C (Munzing Chemie GmbH)	0.2	30 min	
Sodium bicarbonate	0.7	3 x 10 +	The pH of the cross section of the leather was
Water for dilution	10	60 min	found to be 3.8.
Washing			
Water	200	10 min	Bath was drained.

Leathers were hooked for drying. The dried leathers were conditioned, staked, dry shaved to a uniform thickness (0.6±0.1 mm), trimmed and milled for 3 h. Crust leathers obtained from conventional and reversed process were finished using a commercial semi aniline finish formulation as follows.

Semi-Aniline Finishing

Coating	Chemicals*	Parts	Remarks
1st Coat	Novicolor Pigment Mix	70	4 cross coats given and dried completely
	Roda Bind TU-688/B	120	
	Roda Grand PEG	30	
	Roda Wax Mono	40	
	Roda Wax 944	60	
	Water	680	
2nd Coat	Water	600	One cross coat given and dried completely.
	Roda Lac WG-4	360	
	Roda Feel Microsil	40	
3rd Coat	Water	880	One cross coat a given and dried completely. Dry milled, toggled and finiflexed.
	Roda Feel Microsil	120	

*All the chemicals were procured from TFL Ltd., India.

Chromium Content and Shrinkage Temperature of Wet Leathers

Samples from the official butt portion of experimental (wet processed stage) and control wet blue leathers were taken for chromium estimation.[20] A known weight (~1g) of the sample was taken and the amount of chromium was estimated as per standard procedures.[21] Samples were initially analyzed for moisture content and chrome content was expressed on dry weight basis of leather.[22] The shrinkage temperature of the leathers was measured using a Theis shrinkage tester.[23]

Physical and Chemical Properties of Finished Leathers: Evaluation for Military Specifications

A set of turn-key tests were carried out at Texas Tech University to verify whether the reverse processed leathers meet the military specifications. Specification for military gloves for flyer's summer applications was chosen for comparison.[24] The gloves covered by this specification are intended to be worn by flying personnel in the warm temperature zones. All the tests were conducted in accordance with American Society for Testing and Materials (ASTM) standards.[25] Four leathers each from control and reverse processed finished leathers were subjected to the tests and the average values of four measurements were obtained.

Physical Testing and Hand Evaluation of Leathers

Samples for various physical tests from experimental and control finished leathers were obtained as per IUP method.[20] Specimens were conditioned at 80±4°F and 65±2% relative humidity over a period of 48 h. Physical properties such as tensile strength, % elongation at break and stitch tear strength were examined as per the standard procedures.[26,27] Finished leathers from control as well as experiment were assessed for softness, run, grain smoothness and general appearance by hand and visual examination. The leathers were rated on a scale of 0–10 points for each functional property by two experienced tanners, where higher points indicate better property.

Analysis of Chromium in Spent Liquors

Chrome liquor collected from the control chrome tanning process was analyzed for chromium content as per the standard procedure.[28] In the case of reversed leather process, the final liquor was collected and used for the chromium analysis. The uptake of the chromium was calculated based on the amount of chromium present in the spent liquor and the amount chromium offered for processing.

Analysis of Composite Waste Liquor

Composite liquors from control and experimental processes were collected from all the unit processes except pretanning processes (soaking to deliming/degreasing) and analyzed for COD and TS (dried at 103–105°C for 1 h) as per the standard procedures.[29] From this, emission loads were calculated by multiplying concentration (mg/L) with volume of effluent (L) per metric ton of raw sheepskins processed.

Scanning Electron Microscopic Analysis

Samples from the control (C) and experimental (E) finished leathers were cut from the official sampling position.[20] The leather samples from both experimental and control process with uniform thickness were directly taken for analysis without any pretreatment. Quanta 200 series scanning electron microscope was used for the analysis. The micrographs for the grain surface and cross section were obtained by operating the SEM at low vacuum at an accelerating voltage of 14 KV with different magnification levels.

Chromium in Finished Leathers Using X-Ray Fluorescence (XRF) Spectrometer

Samples from control and experimental finished leathers were obtained from the official sampling position.[20] Samples from control and experimental processes were analyzed for chromium using standard acid digestion method.[25] Composite-type as well as intact leather samples were prepared for the XRF analysis. The composite-type was ground leather (Fritsch mill) that was pressed into a pellet (Carver press + custom die) for the XRF auto sampler. The intact samples were used as such, but cut to size of the cups in the auto sampler. Three different aliquots were prepared for each category of samples except for the composite where only one sample was made. A Twin-X Benchtop XRF Spectrometer with PIN diode detection system from Oxford Instruments was used. The averages of 5 separate measurements for each of the aliquots were obtained and calculated by the instrument. The relative standard deviations (%) were calculated manually.

RESULTS AND DISCUSSION

Chromium in Wet Leather and Spent Tan Liquor

As can be seen in Table I, the leather from the reversed process contains more chromium than the control leather. This may be due to the presence of post-tanning organic chemicals during chrome tanning in the reverse process. Since the offer of chrome is the same in both processes, the uptake of chrome in the reversed process is significantly greater than in the conventional process. The shrinkage temperature of leathers from both processes is greater than 120°C indicating no benefit from the extra chrome in the reverse process leather thereby paving way for reducing the chrome offer in the reverse process. These results are in accordance with the earlier literature.[19]

TABLE I
Comparison of Chromium Content and Shrinkage Temperature of Wet Leathers and Percentage Exhaustion of Chromium from Conventional (C) and Reversed (E) Processes

Sample	% Cr_2O_3 (dry weight basis[a])[b]	% Uptake of chromium[b]	Ts (°C)
C	2.98±0.10	60±2	>120
E	3.86±0.08	81±2	>120

[a]moisture free tanned leather weight

[b]Average of three measurements along with standard error

TABLE II
Comparison of Performance of Finished Leathers from Control and Experimental Processes

Parameters	Control[a]	Experimental[a]	MIL-DTL-81188C[23]
Chromic oxide (%)	3.17±0.12	4.27±0.12	-
pH	4.48±0.34	3.70±0.26	-
Ts (°C)	> 120	> 120	-
Chloroform extractables (%)	17±0.4	23±0.7	-
Wet crocking	1-2	2	-
Dry crocking	2-3	2-3	-
Shrinkage to perspiration (%)	9.1±1.7	7.2±1.3	<15
Staining	1	2	>4
Shrinkage to washing (%)	4.7±1.3	9.5±3.7	<20
Stiffness, ° torsion	40.5±0.8	40.8±1.1	<60
Resiliency, ° torsion return	1.9±0.08	2.2±0.1	
% Elongation until 25 lbs	46.8±2.5	44.9±2.6	>25
Stitch tear (lb)	10.0±1.8	15.3±1.2	>12

[a]Average of four measurements along with standard error; For some parameters, standard error values were not available.

TABLE III
Chromium Content in Finished Leathers from X-ray Fluorescence Analysis

	Control	Experimental
ASTM (%)	3.17	4.27
RSD	1.01	0.66
XRF Composite, (%)	3.18	4.22
RSDa	-	-
XRF Intact, (%)	3.21	4.21
RSD	4.36	3.01

[a]RSD was not calculated as only one sample was made.

Performance of Leathers for Military Flyer's Glove Applications

Various performance oriented physical and chemical properties of finished leathers from control and reverse processes are shown in Table II, along with the specification for military flyer's glove leather. It is seen that the amount of chromium in both control and reverse processed leathers is higher than the values obtained at wet condition, as shown in Table I. This may be due to the difference in the moisture content between wet and finished leathers. Reverse processed finished leathers contain more amount of chromium than control finished leathers similar to the trend seen during wet blue stage. Chloroform extractables seem to be slightly more in reverse processed leathers. Wet and dry crocking behavior is almost similar for both control and reverse processed leathers. Other requirements for military gloves such as shrinkage to perspiration, shrinkage to washing, stiffness, stitch tear and % elongation are within the values specified in the standard for both control and reverse processed leathers.[24] Staining values for both control and reverse processed leathers do not meet military glove requirements, which may be due to improper choice of the dyestuff. In general, the performance of reverse processed finished leathers is comparable to control leathers and complies with the standard for military flyer's glove applications assuming that proper dyes would be deployed.

X-Ray Fluorescence of Leathers: A Rapid Chromium Assay

In this investigation, X-ray fluorescence analysis was carried out for rapid analysis of chromium in finished leathers. Composite and intact samples were analyzed in order to verify whether non-destructive testing is feasible. Standard acid digestion based ASTM analysis was also carried out for comparison. The chromic oxide content in control and reverse processed finished leathers using all these analyses is shown in Table III. It is seen that reverse processed leathers show higher chromic oxide content than control leathers in all three measurement types, ASTM standard, XRF composite and XRF intact. The values are realistically similar among all three measurement types indicating XRF analysis can be used for measuring chromium in leathers rapidly without destroying leather matrix.

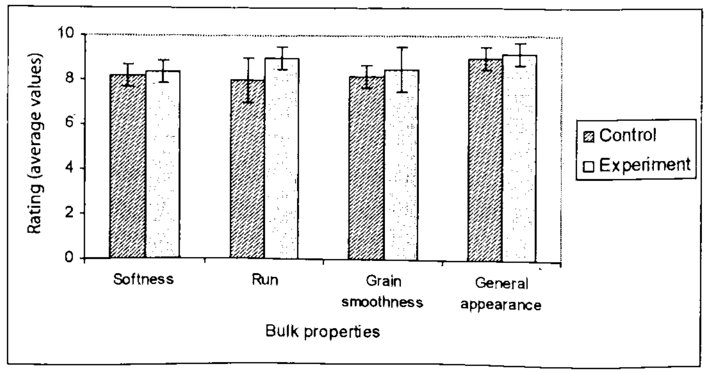

Figure 2: Evaluation of organoleptic properties of finished leathers obtained from control (C) and experimental (E) process

Physical Characteristics and Hand Evaluation of Leathers

The average strength values of five leathers each from conventional and reversed process are given in Table IV along with standard error. It is seen that both the strength properties of leathers obtained from the reversed process are better compared to conventionally processed leathers. These results are in agreement with that observed during the performance analysis. The average rating of bulk properties for the five leathers from control and experiment, evaluated by two independent tanners, were calculated for each bulk property and given in Figure 2. Softness, run, grain smoothness and general appearance of the leathers from reversed process are slightly better than conventionally processed leathers. This may be due to improved uptake of post tanning and tanning chemicals in the reversed process.

Scanning Electron Microscopic Analysis

The scanning electron micrographs of finished leather samples from conventional and reversed processes showing the grain surface at a magnification of ×100 are shown in Figures 3a and 3b. The grain surface and hair pores of both control and experimental leather samples are clean. In other words, reversing the order of conventional process does not lead to any deposition of chemicals used for post tanning and tanning. Scanning electron micrographs of finished leather samples from conventional and reversed processes showing the cross section at a magnification (×150) are given in Figures 4a and 4b. It is seen that the orientation of fibers is uniform and regular in both control and experimental samples. Higher magnification (×500) scanning electron micrographs (Figures 4c and 4d) show a well separated fiber structure in experimental sample compared to control sample. This may be due to higher uptake of post tanning chemicals in general and fatliquor in particular.

a b

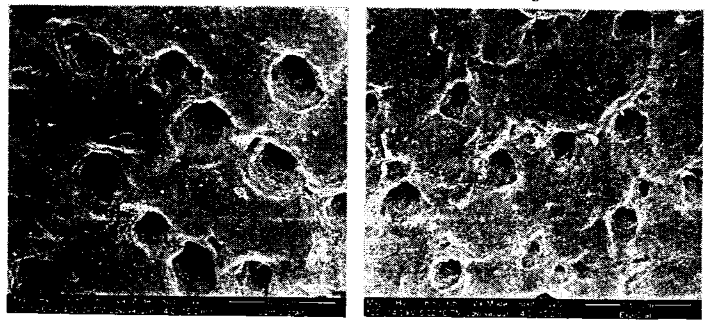

Figure 3: Scanning electron micrographs of finished leather samples showing the grain surface at ×100 magnification
a) control and b) experimental

TABLE IV
Physical Strength Data of Finished Leathers from Control (C) and Reversed (E) Process

Sample	Tensile strength (kg/cm2)	% elongation at break	Stitch Tear strength (kg/cm)
	Average value[a]	Average value[a]	Average value[a]
C	138±8	48±2	27±2
E	152±6	54±3	32±2

[a]Average of mean of five measurements of along and across backbone values along with standard error

TABLE V
Water Consumption and Discharge for Conventional and Reversed Leather Process for Processing 1 kg of Raw Hair Sheepskins[a]

	C		E	
Unit processes	Input (L)	Output (L)	Input (L)	Output (L)
Pickling	0.700	0.350	-	-
Chrome tanning/reversed process	0.350	0.680	0.350	0.340
Washing	1.400	1.400	1.400	1.380
Washing	0.466	0.270	-	-
Neutralization	0.233	0.230	-	-
Washing I	0.466	0.460	-	-
Washing II	0.466	0.460	-	-
Retanning, dyeing and fatliquoring	0.233	0.240	-	-
Washing	0.466	0.460	-	-
Dilution of acids/alkalis and emulsification of fatliquors	0.220	0.220	0.300	0.290
Total	5.000	4.77	2.050	2.010

[a]Weight of sheepskins before soaking

TABLE VI
Composite Liquor Analysis[a]

Process	COD (ppm)[b]	TS (ppm)[b]	Volume of effluent (L/metric ton of raw skins[c])	Emission load (kg/metric ton of raw skins[c] processed)	
				COD	TS
Control	5990±18	51334±32	4770	28.6	245
Experimental	6795±22	36900±36	2010	13.6	74

[a]Composite liquors were collected from all the unit operations expect from soaking to degreasing
[b]Average of three measurements along with standard error
[c]Weight of hair sheepskins before soaking

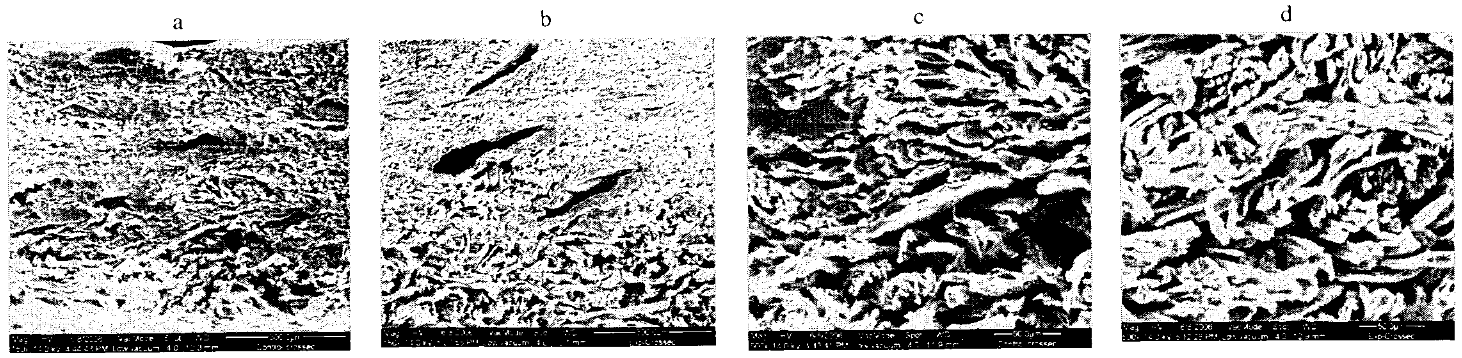

Figure 4: Scanning electron micrographs of finished leather samples showing the cross section at lower and higher magnifications a) control (×150) b) experimental (×150) c) control (×500) and d) experimental (×500)

Water Audit

It is expected that the reversed leather process would enable significant reduction in water usage since the process avoids several acidification, deacidification and washing steps. Hence, water consumption and discharge audit for conventional and reversed process has been carried out. The quantity of water consumption and discharge for processing 1 kg of raw hair sheepskin through conventional and reversed process is given in Table V. It is apparent that reversed process enjoys a reduction in water consumption and effluent discharge by 59 and 58% for processing 1 kg raw sheepskin. It has been reported that, by 2025 AD, 1.8 billion people will live in countries or regions with absolute water scarcity.[30] In this context, the potential of reversed process for reducing water consumption is remarkable.

Environmental Benefits

The composite liquors were collected from all unit processes except from soaking, liming and deliming/degreasing. Two environmental parameters such as COD and TS have been chosen to analyze the environmental impact of conventional and reversed leather processes. A direct comparison of the observed COD and TS values may not give proper results on the environmental impact. Hence, these values have been converted into emission loads. The COD and TS values and the corresponding calculated emission loads are given in Table VI. It is interesting to note that the concentration of TS is significantly lower in the effluent from reversed process compared to conventional process, in spite of low volume of effluent generation. This is primarily due to the fact that reversed process avoids several acidification-deacidification steps that are followed in conventional leather processing. It is known that acidification-deacidification steps would lead to the formation of neutral salts that contribute to dissolved or total solids. It is seen that COD value of effluent from the reversed process is slightly higher than conventional process. This is due to the presence of pollutants in significantly low amount of effluent. It is seen that there is a significant reduction in COD and TS parameters when they are converted into emission loads. The reduction in COD and TS loads are 53 and 70%, respectively. These reductions are not only due to elimination of several processes but also due to better uptake of chemicals such as chromium, syntans, dyes and fatliquors. It is intriguing to note that these reductions are possible without using any specialty chemicals.

Techno-Economic Viability

In this work, reversed leather process has been explored to achieve reductions in water, time, power as well as better quality of leather and effluent. It is already shown (Table V) that reversed leather process enjoys a reduction in water consumption by 59% compared to control process, which provides savings in water cost. This reduction in water consumption lowers the hydraulic load by 58%, thereby reducing the operating cost of effluent treatment plant (ETP). The consumption of process time and power for control and experimental processes is given in Table VII. Time consumption for reversed process (drumming time) is 42% lower than control process. Further, there is also a significant reduction in time lag between conventional chrome tanning/wet finishing and reversed process, which is usually a minimum of 12 hours (overnight ageing). The reduction in energy consumption for reversed process leads to a saving of about US$ 20 for processing 1 metric ton of raw hair sheepskins. The total reduction in chemical consumption (Table VIII) is about 39% for processing 1 metric ton of raw sheepskins through reversed process. The chemical costing was not carried out for BCS, syntans, dyes and fatliquors because there is no change in type and percentage offer of chemicals between the two processes. However, the reversed process provides a considerable reduction in chemical cost by about US$ 14 for processing 1 metric ton of raw sheepskins by avoiding acids and alkalis required for several acidification and deacidification processes. Hence, it is evident that there is a significant reduction in the consumption of water, time, energy and chemicals. This would provide an overall reduction in the cost of reversed leather processing.

TABLE VII
Time and Power Consumption for the Conventional (C) and Reversed (E) Processes

Unit operations	Time (h) C	Time (h) E
Pickling	1.50	-
Chrome tanning/reversed process	5.83	9.91
Washing	0.16	0.16
Washing	0.16	-
Neutralization	3.08	-
Washing I	0.16	-
Washing II	0.16	-
Retanning, dyeing and fatliquoring	4.75	-
Fixing	1.33	-
Washing	0.16	-
Total	17.29	10.07
Total power consumption (kwh)	518.7	302
Cost (US$)	48.4	28

@1 h running = 30 KWh; 1 KWh = US$ 0.1

TABLE VIII
Comparison of Chemicals Consumption for Conventional (C) and Reversed (E) Leather Processes

Chemicals	C (kg/metric ton of raw hair sheepskins processed)	E (kg/metric ton of raw hair sheepskins processed)
Sodium chloride	70	-
Sulfuric acid	8.4	-
Basic chromium sulfate	56	56
Sodium formate	9.3	-
Sodium bicarbonate	8.4	5.04
Ammonium bicarbonate	3.45	-
Syntans	11.65	11.62
Dyes	7.0	7.0
Fatliquors	56	56
Formic acid	4.7	7.0
Total	235	143

CONCLUSION

In this work, a reversed leather processing method has been followed for making military glove leathers from hair sheepskins. A significant increase in chromium uptake in the leather is observed for reversed process. This is confirmed through X-ray fluorescence analysis. The performance properties required for military glove application of reverse processed leathers are comparable to conventionally processed leathers. Both control and experimental leathers meet the specifications except for staining. Leathers obtained from reverse process possess slightly better physical as well as bulk properties to that of leathers from conventional process. Scanning electron micrograph reveals that leathers from reversed process seem to be more opened fiber structure compared to conventionally processed leathers. Further, the reversed process technique results in remarkable reduction in pollution loads such as COD and TS by 53 and 70%, respectively. More particularly, the water usage is reduced by nearly 59% for processing one metric ton of raw sheepskins from delimed/degreased to crust stage, which is one of the pioneering achievements. The reversed process also reduces the usage of chemicals by 39%. Techno-economic viability study shows that there is a considerable reduction in cost of leather production and the process is commercially viable. Hence, this investigation provides an alternative process for making military glove leathers with improved performance and low eco-impact compared to conventional leather process.

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