Integrated Chrome Free Upper Leather Processing-Part-II: Standardization and Evaluation of Vegetable - Aluminium Tanning System

by

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Abstract (In English and Spanish)

In our earlier work, Vegetable-Aluminium (Veg-Al) combination tanning system was found to be suitable for the manufacture of integrated chrome free upper leather. This paper describes our efforts in the optimization of integrated upper leather processing. The physical strength properties, techno-economic feasibility and environment impact assessment studies of the integrated process in comparison with conventional upper leather processing from chrome tanning have also been carried out. The offer of post tanning auxiliaries viz., syntans and fatliquors is optimized based on the organoleptic properties of the leathers obtained. The integrated process and the leathers thereof were compared with upper leather processing and leathers from conventional chrome tanning respectively. The integrated process resulted in more than 60% saving of water compared to the conventional upper leather processing from chrome tanning. The experimental process has benefits in terms of improved productivity and decreased production cost due to reduced water, time, power and labor utilization resulting from the integration of process.

Nuestro trabajo anterior, en un Sistema de Curtición combinado Vegetal-Aluminio(Veg.-Al) se encontró ser adecuado para el procesamiento integral de cuero exento de cromo para capelladas. Esta publicación describe nuestros esfuerzos en la optimización del procesamiento integral de cuero exento de cromo para capelladas. Las propiedades físicas de resistencia, la factibilidad técnico-económica y la evaluación de las consecuencias ecológicas de este sistema integral de procesamiento fueron comparadas con los resultados del proceso convencional de fabricación de cuero al cromo para capelladas. La oferta de recurtientes v.g. curtientes sintéticos y engrases son optimizables por sus efectos sobre propiedades palpables del cuero resultante. El proceso integral y sus resultados fueron comparados con el procesamiento de cuero para capelladas y capelladás curtidas al cromo por medios convencionales respectivamente. El integral resulto en un 60% de ahorro de agua en comparación a la producción convencional de cuero para capelladas al cromo. El proceso experimental goza de beneficios en términos de aumentada productividad y disminución de costos debido a la reducción de agua, tiempo, potencia, y mano de obra utilizada como resultado de la integración del proceso.

Introduction

Currently more than 90% of upper leathers are manufactured using chromium as the main tanning agent because chrome tanning results in leathers with high hydrothermal stability, good strength characteristics and organoleptic properties, good affinity and compatibility with dyes, retanning materials, fatliquors, and finishing auxiliaries. In recent times, leather manufacturers are looking for alternative tanning systems. Also there is increased pressure to reduce water consumption in leather processing industries. The state of Tamilnadu where 60% of the total Indian leather production is taking place, at present suffers from depletion of water resources. Hence, it is important for the leather industry to equip itself with alternative technologies where minimal water is required for leather manufacture. Hence there is an imperative need for cost effective innovative leather processing techniques for the sustenance of the leather industry. Earlier we have developed an integrated upper leather processing using Veg-Al tanning system where we demonstrated that upper

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TABLE I
Integrated Veg-Al Upper Leather Processing
(% Chemical Addition Based on Pelt weight)

Process	Chemicals	%	Duration (Min.)	Remarks
pH adjustment	Pickle liquor	50		
	Sodium bicarbonate (1:10 dilution with water)	1.0	3x15	pH increased to 4.5-4.7;
	Water	50		
	Basyntan P (Phenolic syntan)	2	30	
Vegetable Tanning	Wattle	7	60	
	Wattle	7	60	
	Myrobalan	2	30	
Aluminium Retanning	Lutan BN (Aluminium syntan)	4	60	
Basification	Sodium bicarbonate (1:10 dilution with water)	1.0	3x15	pH increased to 4
Retanning, Dyeing and Fatliquoring	Water	35		
	Sellasol PR (Protein syntan)	4	30	
	Dermolix ESO (Acid stable synthetic fatliquor)	3	30	
	Acid dye	1.5	40	Check penetration
	Dermolix ESO	2	30	
	Distan FPF (Formaldehyde free phenolic syntan)	4	30	
Fixing	Formic acid	1	3x15+30	Drain
Washing	Water	100	10	Drain, Pile O/N, Set, Dry, Stake, Dry-shave, Trim & Buff

leather can be made in one step from pickling.[1] However the process was not optimised to obtain good quality upper leathers. Especially there was scope for improving the light fastness of leather and optimizing the offer of post tanning auxiliaries viz., syntans and fatliquors. The integrated upper leather processing has to be evaluated for the leather characteristics, techno-economic feasibility and environmental impact. Hence this paper focuses on the optimization of integrated upper leather processing to obtain better leathers and also to compare the techno-economics and environmental impact with the currently practised chrome tanning processes and the resultant leathers, respectively.

EXPERIMENTAL

The raw material used for leather processing was pickled goatskins made from wet salted goat skins selected in the weight range of 1kg. The chemicals used for leather processing were of commercial grade. The chemicals used for analytical techniques were of laboratory grade.

Integrated Upper Processing

Pickled goat skins were processed into upper leather employing the process given in Table I.

Optimisation of Post Tanning Processes

The post tanning for the Veg-Al combination system is optimized by varying the amount of syntans and fatliquors. Experimental trials were carried out by varying the amount of syntans as 6, 8 and 10% with constant fatliquor offer of 4% employing the process given Table I. Similarly experimental trials were also carried out to optimize the offer of fatliquors by varying the amount of the same as 4, 6 and 8% with a constant syntan offer of 6%.

Studies on Dyeing Characteristics of One Step Upper Leathers

In order to study the dyeing characteristics of the upper leather from integrated upper processing, experimental trials were carried using different dyes viz; acid and metal complex dyes for the Veg - Al using the optimized integrated upper leather processing. During the processing, the penetration of dyes was monitored visually and the time

TABLE II
Control - Upper Crust from Conventional Chrome Tanning System

Process	Chemicals	%	Duration (Min.)	Remarks
Tanning	Pickle Liquor	50		(% chemical addition is based on pelt weight)
	BCS	8	120	
	Water	100		
	Sodium formate	1	60	
	Sodium bicarbonate (1:10 dilution with water)	1.25	3X15 + 60	pH increased to 4.0; Drain
Washing	Water	100	10	Drain, piled and aged for 2days; sammed. (% chemical addition for subsequent operation based on sammed weight)
Wetting back	Water			
	Surfactant	150	0.5	Drain.
Acid wash	Water	100		
	Acetic acid	1	60	
Rechroming	BCS	6	120	
	Sodium bicarbonate	1.5		
	Water	15	3X15+45	pH adjusted to 4.0; Drain/Wash/Drain; Piled O/N
Neutralization	Water	150		
	Sodium bicarbonate	1.5		pH adjusted to 5;
	Water	15	3X10 + 30	Drain/Wash/Drain
Retanning, Dyeing and Fatliquoring	Water	150		
	Sellasol PR	4	30	
	Wattle	6	2X30	
	Distan FPF	3	30	
	Dermolix ESO	3	30	
	Acid dye	3.0	40	Check penetration
	Balmol SXE (Synthetic fatliquor)	4	30	
	Distan FPF	5	2X30	
Fixing	Formic acid	1.5		
	Water	15	3X15+15	Drain
Washing	Water	100	10	Drain, Pile O/N, Set, Dry, Stake, Dry-shave, Trim and Buff

required for the complete penetration was noted. The experimental upper crusts were evaluated for the light and rub fastness and compared with the chrome tanned upper control leathers.

Comparison of Experimental One Step Upper Leather Processing with Control Upper Trials

Four pickled goat skins of similar weight range of ~1 Kg/skin (wet salted weight) were taken for comparing the integrated upper processing with chrome tanned control upper leathers. The four left halves were processed using optimized Veg-Al integrated upper leather processing. The % chemicals employed for the integrated process is based on pelt weight (after fleshing). Four right halves were used for processing control trials of chrome tanning system and subsequently post tanned into upper crust leathers (process given in Table II). The % chemicals employed for the control processing upto tanning is based on pelt weight and after tanning the wet blue leathers were sammed and post tanned without shaving. The % chemicals employed for the post tanning of control processing is based on sammed weight. The leathers from control and experimental process were compared for physical strength and organoleptic properties. The process of the control and experimental trials were compared for their techno-economic feasibility. The waste liquor of the control and experimental processes were compared for their environmental impact.

Evaluation of Physical Testing and Organoleptic Properties of Leather Samples

The upper leathers made using integrated process and chrome tanned control process were determined as per standard procedures. The samples for physical testing were obtained as per IULTCS method.[2] Eight samples from four left halves leathers corresponding to experimental and eight samples from corresponding right halves of the control chrome uppers were evaluated for physical strength properties. Tensile strength, tear strength and grain crack strength were examined as per the standard procedures[3-5] and are reported with standard deviations. Organoleptic properties of the leather samples were evaluated as reported previously.[1]

Chemical testing

Determination of chemical oxygen demand (COD) and Total dissolved solids (TDS) were carried out using standard methods.[6] Estimation of aluminium content in the effluent liquor was carried out by Atomic absorption spectrophotometer using the standard methods of analysis of wastewater.[6] Chromium in spent chrome liquor was estimated by spectrophotometric technique.[7] Triplicate samples were used for each analysis.

Colour and Light Fastness Measurements

Colourfastness to rubbing was done using circular rub fastness tester for the experimental and control upper crust leathers, to study the dyeing behavior of acid and metal complex dyes. The leathers were compared with grey scale reading of 1-5 (1-corresponding to very poor color fastness and 5- corresponding to very good color fastness). Light fastness measurements were carried out as previously reported.[1]

Results And Discussion

In our earlier paper,[1] an offer of 16% wattle and 4% aluminium syntan was established as the optimimum tanning system. In the current paper, minor variation in tanning is incorporated in order to prevent oxidation of the wattle by using myrobalan. It is well established that myrobalan (hydrolysable tannin) topping after tanning with wattle prevents photo oxidation. Hence in the current process 2% of wattle (16%) in the original experiments is replaced with myrobalan and the resulting leathers has been found to possess better light fastness characteristics.

Optimization of post tanning of Veg - Al system for integrated upper process

As the use of excess amount of the syntan and fatliquor will result in unnecessary loss of chemicals and increase in the p ollution load of the effluent, the amount of syntan and fatliquor offered should be optimized. The reduced offer of the syntan and fatliquor may result in inadequate leather properties and hence post tanning process has to be optimized for the judicious usage of the auxiliaries viz., syntans and fatliquors. Since mimosa tannin has been used for tanning, which is known to result in fuller leathers, the experimental trails have been carried with low offer of syntans viz., 6, 8 and 10%. The organoleptic properties of leathers processed using Veg - Al with varying syntan and fatliquor offer are shown in Table III. From the table, it is seen that there is a marginal increase in fullness and roundness of the leathers treated with 10% syntans as compared to 6 and 8% offer of syntan; however there is a slight decrease in grain tightness observed with higher offer of syntans and hence 6% offer of syntan is considered to be the optimum enough for making upper leather through this compact process. In order to optimize the % offer of fatliquor, leathers made with different amounts of the fatliquor viz. 4, 5 and 6% is used at a constant 6% offer of syntans and the organoleptic properties of the leather are given in Table III. From the table, it is clearly seen that fatliquor offer of 4% is sufficient to obtain upper leathers as this offer of fatliquor has resulted in leathers with better fullness, roundness and grain tightness. It is observed that 6% syntan and 4% fatliquor offer (% based on pelt weight) is adequate for obtaining upper leathers with good organoleptic properties and hence the same are considered to be optimum.

TABLE III

Organoleptic Properties of Leather Processed by Veg - Al syntan with Different % Offer of Syntan & Fatliquor (Scale 0-10)

Experiment	% offer	Fullness	Roundness	Grain tightness
% Syntan offer*				
	6	8	7.5	7.5
	8	8	7.5	7.5
	10	8.5	7.5	7
% Fatliquor offer **				
	4	8	7.5	7.5
	5	8	6	7
	6	8	5	7

* - 4% Fatliquor offered ** - 6% Syntan offered
Standard Deviation < ±0.5

TABLES IVa and b

Comparison of Dyeing Characteristic of Experimental (Optimized Integrated Process) and Control (Chrome) Tanned Upper Crust Leathers

TABLE IVa: Light fastness (Scale1-8)

Experiment	Light fastness	
	Acid dye	Metal complex dye
Veg - Al (Experimental)	6±0.0	6.5±0.5
Full-Chrome (Control)	6.5±0.5	6.5±0.5

TABLE IVb: Color rub fastness (Scale 1-5)

Experiment	Acid dye		Metal complex dye	
	Wet rub	Dry rub	Wet rub	Dry rub
Veg - Al	4±0.0	4.5±0.5	4.5±0.5	5±0.0
Control	4±0.0	5±0.0	4.5±0.5	5±0.0

TABLE V

Physical Strength Characteristics of Optimized Veg-Al Integrated Upper Crusts and Control Chrome Tanned Upper Crusts

Experiments	Tensile strength (Kg/Cm²)	% Extension at Break	Tear strength (Kg/Cm)	Grain crack resistance	
				Load(Kg)	Distension(mm)
Veg - Al	256±9	59±3	45±3	39±2	9.3±0.5
Control	260±10	78±4	46±4	40±2	13.6±0.4
BIS standards[8]	200	40-65	30	20	7

* - Eight samples used for each measurement

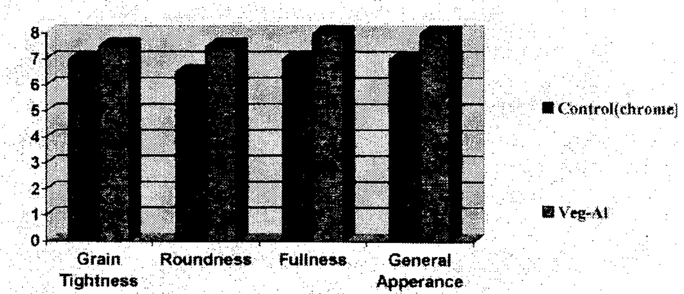

Figure 1. - Organoleptic properties of the upper crust leathers processed by experimental (Veg-Al) and control (chrome) trials (S.D. < ±0.5)

Dyeing Characteristics of One Step Upper Leather

The integrated upper processing is a compact process and it is possible that the chemicals used have a significant influence on the dyes and hence the dyeing property. The dyes used should have good solubility in order to obtain uniform color. Experimental trials using acid dye and metal complex dye have been carried out. During the processing of Veg-Al experimental leathers it is observed that complete penetration of acid dye occurred 40 minutes after the dye (2%) addition, whereas the penetration of metal complex dye took 60-70 minutes. The light fastness and rub fastness of experimental (process as given in Table I with optimised syntan and fatliquor offer) and control leathers processed (Table II) using acid dye and metal complex dye are given in Tables IVa and IVb respectively. From the tables, it is seen that the upper crusts processed using Veg-Al system exhibits comparable rub fastness and light fastness as that of control chrome upper crust leathers.

TABLE VI

Pollution Load of Process Liquor from Tanning to Post Tanning of Experimental Veg-Al Upper Processing vs Chrome Tanned Upper Processing

Parameters	Control (g/Kg)*	Experimental (g/Kg)*
COD	33±1	30±1
TDS	115±3	75±2
Aluminium	-	0.3±0.05
Chromium	6.5±0.3	-

*g per Kg of wet salted goat skin

Strength and Organoleptic Properties of Integrated upper leathers

The strength properties like tensile strength, tear strength and grain crack resistance have been studied on leathers processed with control chrome tanning and integrated upper process. The values are given in Table V. From the table, it is observed that the strength properties viz., tensile strength, tear strength and grain crack resistance are comparable to that of chrome tanned leathers. The elongation at break for chrome tanned upper crust leathers were as high as 78% compared to an elongation of 59% for upper crust leathers processed by integrated tanning system. The experimental leathers processed by the integrated upper processing have been found to possess physical strength characteristics comparable to the control leathers and better than the norms prescribed by BIS standards for upper leathers.[8] The organoleptic properties of the control and experimental upper leathers has been evaluated by three experienced tanners to a point scale of 0 to 10 and the average values are sown in the form of graph in Figure 1, the deviation in values of the evaluation between one tanner and another was less than 0.5. From the figure it is clearly seen that the organoleptic properties of experimental leathers are comparable to that of the control upper crust leathers processed by a conventional chrome tanning process.

TABLE VII

Comparison on Amount of Water Used (from pickle to crust) for Control and Experimental Processing of Goat Skins of 1kg (pelt weight)

Unit Process	Control Litres	Experimental Litres
Tanning	2.65	1.0
Wetting Back, Acid wash, Rechroming & Washing	1.65	-
Neutralization & Washing	1.25	-
Retanning, dyeing, fatliquoring and Washing	1.25	1.65
Total	6.8	2.65

TABLE VIII
Comparison of Time for Control and Experimental Processing of Pickled Goat Skins into Upper Crust Leathers

Control		Experimental	
Unit Process	**Time (Hrs)**	**Unit Process**	**Time (Hrs)**
Chrome Tanning and Basification	4.0	pH adjustment	0.75
Ageing	48.0	Pre tanning	0.5
Wetting back and acid wash	2.0	Vegetable tanning	2.25
Rechroming, basification and washing	2.3	Aluminium tanning and basification	2
Ageing	24		
Neutralization and washing	1.8		
Retanning, dyeing and fatliquoring	4.2	Retanning, dyeing and fatliquoring	5.0
Washing	0.3	Washing	0.3
Total	87.4		10

TABLE IX
Comparison (from pickling to crusting) of Water, Power and Cost (water & power) for Conventional and Experimental Leather Processing of 1 ton of Goat Skins

Water (litres)		Power (Kwh)^		Cost (Water* + Power#) in US$	
Cont	Expt	Cont. (15.4hrs Drumming time)	Expt. (10 hrs Drumming time)	Cont	Expt
6800	2650	462	300	72.5	42

^ - For running drum of capacity 1000kg per hour, power consumption is 30 Kwh
* - Cost of 1000 litres of water at Tamilnadu, India is equivalent to US$ 2.5
# - Cost of 1 Kwh of power at Tamilnadu, India is equivalent to US$ 0.12

Environmental Impact of the One Step Upper Process

The effluent load (tanning and post tanning liquor) of the process liquor from chrome tanning and the experimental Veg-Al tanning system are given in Table VI. COD values of control and experimental process have been found to be comparable. The COD load is 33g/kg (based on wet salted weight) for control chrome tanning system, whereas as Veg-Al tanning system resulted in a COD load of 30g/kg. The presence of vegetable tannins in the effluent of experimental leathers is the major source of COD, whereas the conventional chrome tanned leathers requires more amounts of syntans/vegetable tannins to improve the fullness of the leather and a possible lower exhaustion of chemicals could possibly have contributed to slightly higher load of COD. The TDS load generated from the control processing of chrome upper crust is found to be higher than experimental Veg-Al integrated upper process. The major advantage with respect to experimental process is that there is no discharge of chromium, however 0.3 g of aluminium is found in the effluent for processing one kg of raw material processed. In the control system around 6.5g of chromium is found to be discharged for one kg of raw material processed.

Water Reduction

A comparison on the amount of water used for processing of upper leathers by chrome tanning and experimental Veg-Al one step upper processing from pickled goat skins is made and the same is given in Table VII. From the table, it is seen that in the experimental processing employing Veg - Al combination for making the upper crusts, there is a saving of more than 60% of water compared to the chrome tanned upper leather system (tanning and post tanning have been taken for comparison).

Techno-Economical Advantages of One Step Upper Manufacture

The integrated tanning-post tanning process has been followed in this work aiming at the reduction in water, time, power consumption and in pollution reduction without compromising the quality of leathers. Comparison of time taken for conventional chrome tanned upper leather system and integrated upper system is shown in Table VIII. It is seen from the table that experimental process requires only one seventh of the time required for processing with a conventional chrome tanned system.

Comparison of the power consumption and cost due to power and water of conventional chrome tanned process and integrated upper process is made and shown in Table IX. Only 10 hours of drumming is required for the experimental process whereas the conventional process requires 15.4 hrs of drumming time and hence more consumption of power. There is a net saving of US$30.5 alone due to the savings in the water and power for processing one ton of goat skins. Comparing the process between the pickled to upper crusting, there is a total reduction in time by 88% for the experimental process as compared to control process and hence a considerable reduction in the manpower charges is expected. Savings due to reduced manpower charges, reduced treatment cost for handling less volume of effluents, etc. will result in huge savings for the leather manufacturers along with above quantified savings. Apart from this, the productivity of a manufacturing unit processing upper leathers gets improved by 20 - 30% assuming that the unit takes 10 - 11 days for processing the upper leather (conventionally) from soaking to finishing.

Conclusions

The integrated tanning - post tanning process resulted in the reduction in the overall water consumption by 60% as compared to the conventional processing of chrome upper leather (tanning and post tanning). There is a reduction in time by 88% for the one step upper leather process compared to the control process. There is more than 40% reduction in the cost due to less power and water consumption for the one step upper leather processing. More significantly, the quality along with physical strength characteristics of the leathers produced by the integrated processing is found to be comparable to the conventionally processed chrome tanned leather. This work clearly demonstrates the possibility of integrating processing steps in the manufacture of upper leather from skins. However, further work needs to be carried out to illustrate the applicability of this technology in making uppers from hides.

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