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Synergistic Combination Tanning System for Greener Environment towards Sustainable Development in Leather Making

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Abstract **Original Research Article**

Researchers throughout the world are looking for alternative tanning systems to overcome the problems of chromium tanning. Well-documented mineral tannages, like aluminium, silicon, titanium, iron, or zirconium salts. The hydrothermal stability of the leather-tanned using these tanning materials is lower than that of chrome-tanned leather. Pure vegetable tannages are thus not suitable as chrome replacements, whilst combination tannages employing vegetable tannins and metal salts are potential alternatives to chrome tanning, capable of producing hydrothermally stable leathers. In the present study, a combination tanning system based on Quebracho-Aluminum tannage for the production of upper leathers as an eco-friendly process is presented. The Quebracho powder has been used in a combination tanning system based on Quebracho and Aluminum sulphate. Both tanning trials Quebracho followed by Aluminum (Quebracho -Al) and Aluminum followed by Qebracho (Al-Qebracho) have been attempted. Qebracho-Al leathers tanned using 20% Quebracho; followed by 2% Al_2O_3 resulted in shrinkage temperature of 104^{o}C. However, Al-Qebracho leathers tanned using 2% Al_2O_3; followed by 20% Quebracho resulted in shrinkage temperature of 95^{o}C. Qebracho-Al combination system resulted in leathers with good organoleptic and mechanical properties. The work presented in this paper was focused on obtaining an eco-friendly tanning process based on Quebracho-aluminium combination tanning system.

Keywords: Aluminium sulphate, Quebracho, Combination tanning, Shrinkage temperature.

INTRODUCTION

Tanning is the critical process in leather manufacture as it converts a raw hide or skin into leather [1] (Fig-1). Leather is an intermediate industrial product with numerous applications in downstream sectors, such as shoes, clothing, fashion accessories, furniture and many other items of daily use [2] In the tanning process, tanning agent can combine with the -COOH, -NH_2, and –OH groups of collagen to establish a crosslink among collagen fibers, resulting in the enhancement of leather hydrothermal stability [1]. Up to now, chrome tanning agent is still the most widely used one as it can endow the resultant leather with excellent features [3,4] .Chrome tanning causes negative effects on the environment due to the pollution of tannery effluents and improper disposal of chrome-containing solid wastes [5]. With the rising of eco-environmental awareness, chrome-free tanning as an eco-friendly technology has attracted increasing attention [6].

However, other tanning agents such as vegetable tannins, oxazolidine, aluminium, titanium, zirconium have their own disadvantages [7]. Combination tannages are thus considered to be a suitable alternative for chrome-free tanning system. Amongst the innumerable combination tannages that are currently exploited, tannages with vegetable tannins and oxazolidines, or vegetable tannins and aluminium tanning agent are the most promising processes [8,9].

Vegetable tannins are a complex and heterogeneous group of polyphenols widely distributed in plants with very diverse molecular weights ranging from 500 to over 3,000 Da. Depending on the main polyphenolic constituent, tannins are divided into two main groups, condensed and hydrolysable tannins

[10,11].The most common tannins presently used are extracted from chestnut wood, quebracho wood (Fig-2) , tara pods, Chinese and Turkish gallnut, mimosa or wattle bark, oak wood, sumac leaves, and valonia oak acorn [10]. Vegetable tanning agent is considered as a promising alternative owing to its natural origin and appropriate tanning properties [12]. Nevertheless, it also faces several constraints like poor permeability, weak light fastness and difficulty in making pastel shades [13]. Any alternative tanning system should result in leathers with good hydrothermal stability, strength characteristics, organoleptic properties and very importantly eco-friendlier [14].

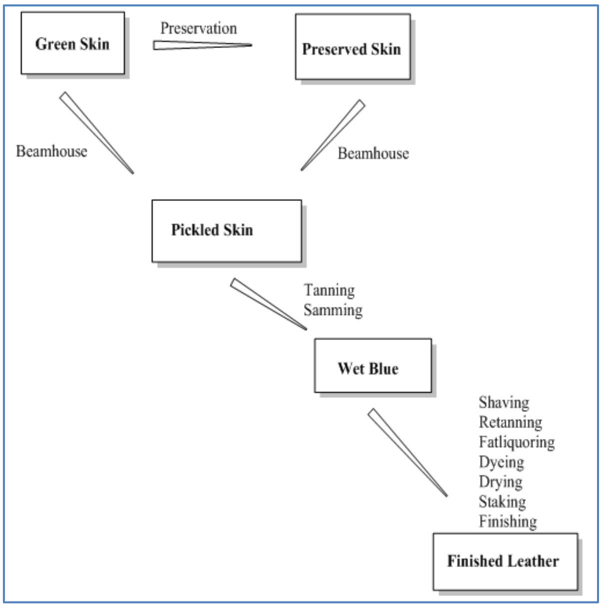

Fig-1: Major Steps of Leather Manufacture

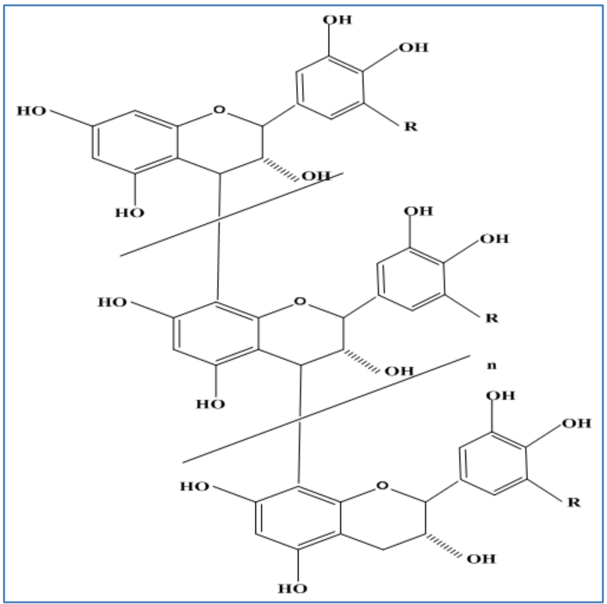

Fig-2: The structure of Quebracho

Quebracho (IUPAC Name: [3,5-dihydroxy-2-(3,4,5-trihydroxybenzoyl)oxy-6-[(3,4,5-trihydroxybenzoyl) oxymethyl]oxan-4-yl] 3,4,5-trihydroxybenzoate, CAS Number: 18483-17-5 Chemical Formula: $C_{27}H_{24}O_{18}$. MW 636.5 [15] is a vegetable tannin extracted from heartwood of the red quebracho, or quebracho colorado (Schinopsis lorentzii), of the family *Anacardiaceae* and is obtained mainly from forests of the Gran Chaco of Argentina, Paraguay, and Bolivia [16]. It is a condensed tannin, not decomposed by acids and gradually polymerizes becoming the insoluble derivative, phlobaphenes. Its use, in this form, is limited to tannage of sole-leather according to the process known as “hot-pitting”. In order to prevent formation of phlobaphanes, the extract is solubilized by heating under pressure with sodium bisulphate (3-8 % on the extract) at 98°C; part of the bonds in tannin are then split. Initially phlobaphanes dissolve, then not only the size of the tannin molecule decreases but changes in the molecule occur which transform it into soluble tannins the main properties of which are rapid penetration into the pelt [17].

Nowadays, there are some chromium-free mineral tanning agents, such as zirconium (IV) [18] aluminium(III), [13] titanium(IV), [19] zinc(II), [20] and iron (III) [21,22]. These alternatives have not been able to replace chromium for various reasons. Aluminium (III) is only a pseudo transition metal ion which forms outer orbital complexes with poor stability resulting in reversible tanning. So conventional aluminum tanning is characterized by its poor wash fastness. It is noted that the combination tannage, like classic vegetable-aluminum combination tannage, is an very effective approach to achieve complementary characteristics. Aluminum-mimosa combination tannage can give wet-white leathers with shrinkage temperature about 100^{o}C [13].

Rao and Nayudamma [23] have extensively studied the vegetable-aluminum combination tannage. In their studies, they have explored both of the tanning options viz., addition of aluminum salts before myrobalan and addition of aluminum salts after myrobalan. Aluminum treatment followed by myrobalan exhibited a shrinkage temperature of 66-69°C, and interestingly, pelts treated with myrobalan followed aluminum resulted in shrinkage temperature of 110-114°C. Whereas, in the case of aluminum tanning followed by wattle (mimosa) tanning results in better leather properties [24]. In the present work, a quebracho - aluminium combination tanning system has been explored towards upper shoe leather making. Our aim is to develop feasible chrome-free tanning technologies to counter ecological constraints and stricter requirements for leather performance properties.

MATERIALS AND METHODS

Materials

Conventional processed pickled goat skins have been taken for tanning trials. Quebracho powder as condensed tannin and aluminum sulphate were used in tanning trials. Chemicals used for post tanning processes have been of commercial grade.

Basic Aluminum Sulphate Solution

A known amount of Aluminum sulphate has been taken in a beaker and 150% of water (% based on the weight of Aluminum sulphate) has been added and the solution stirred for 15-20 minutes, subsequently required amount of ligand (sodium citrate and sodium tartrate) have been added and stirring has been continued for 45 min followed by slow addition of sodium carbonate until the pH has been raised to 3.5. For 0.5M of Aluminum sulphate 0.1M of ligand has been added.

Methods

Combination Tanning Methods

Pickled goat skins have been used for combination tanning trials; Al-Quebracho tanning and Quebracho-Al tanning processes are given in Table 1 and 2 respectively. The amount of Aluminum sulphate used for the tanning trials has been 2% Al_2O_3 in both the experimental processes. A control tanning process has been carried out using Quebracho only as given in Table 3. The post tanning process as mentioned in Table 4 has been followed for experimental and control leathers.

Measurement of Hydrothermal Stability of Leathers

Shrinkage temperature is the most common way to measure hydrothermal stability of leather. Shrinkage temperature of leather is the temperature at which leather shrinks when heated in water and it is commonly related to degree of tannage. At the shrink temperature the sample decreases in length. The shrinkage temperature of control and experimental leathers has been determined using Theis shrinkage tester [25]. 2 X 0.5 cm^2 piece of tanned leather cut from the official sampling position has been clamped between the jaws of the clamp and has been immersed in solution containing 3:1 glycerol: water mixture. The solution has been continuously stirred using mechanical stirrer attached to the shrinkage tester. The temperature of the solution has been gradually increased and the temperature at which the sample shrinks has been measured as the shrinkage temperature of the leathers.

Handle and Visual Examination 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.

Mechanical Properties Test of Leather Samples

Samples for various physical tests from experimental and control crust leathers have been obtained as per IULTCS methods [26].Specimens have been conditioned at $20 \pm 2\,^{o}C$ and 65 ± 2 % R.H over a period of 48 hrs. Mechanical properties such as tensile strength, percentage elongation at break [27], grain crack strength [28] and tear strength [29] have been measured as per standard procedures. Each value reported is an average of four samples (2 values along the backbone and 2 values across the back bone).

Analysis of Spent Tan Liquor

The wastewater of tanning and wet finishing process containing a large number of pollutants was harmful to the environment and human beings. The spent liquor from control and experimental tanning processing were collected, filtered and analyzed for chemical oxygen demand (COD), Biochemical oxygen demand (BOD_5), and total Dissolve solids (TDS) as per standard procedures [30].

Chemical Analysis of Leather Samples

The chemical analysis of the leathers viz. for total ash content, % moisture, % oils and fats, % water soluble, % hide substance, % insoluble ash and degree of tannage were carried out for control and experimental leathers as per standard procedures [31]. Analyses were carried out in triplicates for each sample and the average values are reported.

Table-1: Recipe of the Experimental Quebracho–Aluminum Combination Tanning System for Pickled Goat Skins

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	100	Water		
	0.75	Sodium bicarbonate	3×15	pH 4.5 -4.7
Tanning	2	Phenolic syntan	30	
	10	Quebracho	120	
	10	Quebracho	120	
	2	Al_2O_3 (prepared Aluminium sulphate solution))	90	
Basification	0.75	Sodium bicarbonate	3×15	Check the pH to be 4. Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

Table-2: Recipe of Experimental Aluminum-Quebracho Combination Tanning System for Pickled Goat Skins

Process	%	Product	Duration (min)	Remarks
Pickled pelt	50	Pickled liquor		pH 2.8-3
Aluminum tanning	2	$Al_2\ O_3$ (prepared Aluminum sulphate solution)	120	
Adjustment of pH	0.75	Sodium bicarbonate	3× 15	pH 4.5 -4.7
Vegetable tanning	2	Phenolic syntan	30	
	10	Quebracho	90	
	10	Quebracho	90	
Fixing	0.5	Formic acid	3× 10 +30	Check the pH to be 3.5. Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

Table-3: Recipe of Control Quebracho Tanning Process for Goat Pickled Skin

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	100	Water		
	0.75	Sodium bicarbonate	3× 15	pH 4.5 -4.7
Tanning	2	Phenolic syntan	30	
	10	Quebracho	120	
	10	Quebracho	120	
Fixing	0.25	Formic acid	3× 10 + 30	
Washing	300	Water	10	Check the pH to be 3.5. Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

* - % chemical offer is based on pickled pelt weight of the goat skins

Table-4: Recipe of Post-tanning Process for Control and Experimental Leathers

Process	%	Product	Duration (min)	Remarks
Washing	200	Water	10	
Neutralization	0.75	Sodium bicarbonate	3× 15	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	3× 10 + 30	pH 3.5

* - % chemical offer is based on shaved weight of the tanned leather

RESULTS AND DISCUSSION

Combination tanning methods using Quebracho and Aluminum sulphate were carried out with Al_2O_3 at a concentration of 2% and 20% offer of Quebracho. The shrinkage temperature data of leathers tanned with Quebracho–Al and Al-Quebracho combination along with Quebracho control is given in Table 5**.** From the table it is seen that both the combinations resulted in leathers with better shrinkage temperature than control leathers (Quebracho tanned). The shrinkage temperature of leathers obtained from Quebracho-Al combination tanning is higher than Al-Quebracho. However the combination tanning resulted in leathers with shrinkage temperature of 104°C, which is much better than control Quebracho leather of Ts 84°C. From Table 5, it can be observed that Quebracho -Al combination tanning system resulted in improvement of shrinkage temperature.

Table-5: Shrinkage temperature of control and experimental tanning processes

Experiment	Shrinkage temperature (°C)
Al- Quebracho (2% $Al_2\ O_3$)	95±1
Quebracho -Al (2% $Al_2\ O_3$)	104±1
Quebracho (Control)	84±0.50

* - % chemical offer is based on pickled pelt weight of the goat skins taken
* - 20% Quebracho used for all experiments

Bulk Properties of Leathers - Hand Evaluation of Leathers

Crust leather from both control and experimental processes has been evaluated for various bulk properties by hand and visual evaluation. The average of the rating for the leathers corresponding to experiment has been calculated for each functional property and is given in Fig-3. Higher numbers indicate better property. From the figure, it is observed that Quebracho -Al combination tanned experimental crust leathers exhibited good fullness compared to Quebracho control leathers. The organoleptic properties of the Quebracho-Al crust leathers are better compared to Al-Quebracho crust leathers. This is primarily due to improved penetration and fixation of Quebracho in the experimental process, compared to control process. Other properties such as softness, grain tightness, smoothness, dye uniformity and general appearance are comparable to that of conventionally processed leathers. The general appearance of experimental leathers is better than that of control leathers.

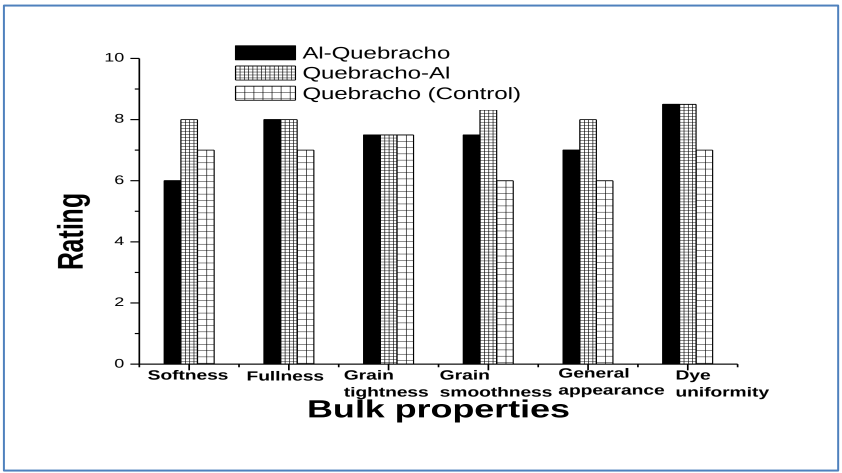

Fig-3: Graphical Representation of Organoleptic Properties of the Experimental and Control leather

Physical Testing of Experimental and Control Crust Leathers

It is necessary to evaluate the physical properties and performance of leather. The physical strength measurements viz., tensile strength, elongation, tear strength, load at grain crack and distension at grain crack were carried out for the control and experimental crust leathers and the data is given in Table 6. It is observed that the tensile strength characteristics like tensile strength, elongation, tear strength of Quebracho-Al tanned crust leathers is found to be higher compared to that of the control and Al-Quebracho tanned crust leathers, whereas load at grain crack and distension at grain crack of both control and Al-Quebracho tanned leathers are found to be lower.

Table-6: Physical Strength Characteristics of Experimental and Control Crust Upper Leathers

Parameter	**Al-Quebracho**	**Quebracho-Al**	**Control (Quebracho)**	**BIS Norms (Minimum Requirements)** [23]
Tensile strength (Kg/cm^2)	223±2	247±3	215±3	200
Elongation at break (%)	57 ±0.70	62±0.80	55±1.50	40-65
Tear strength (Kg/cm)	51±0.60	55±0.70	50±0.80	30
Load at grain crack (Kg)	24±0.70	26±0.80	23±0.60	20
Distention at grain crack (mm)	11±0.80	12±0.80	10±0.60	7

Spent Liquor Analysis

Biochemical oxygen demand (BOD_5), chemical oxygen demand (COD) and Total dissolved solid (TDS) are main parameters in assessing the quality of spent tan liquor The environmental impact analysis of tanning process is assessments of the possible positive or negative impact have on the environmental, social and economic aspects. The COD, BOD_5, and TDS of the spent liquor for experimental and control trials have been determined and are given in Table 7. From the table, it is observed that the COD, BOD_5 and TDS of the spent liquor processed using both the experimental tanning system are lower than the spent liquor from Quebracho tanning (control). The BOD_5 and TDS of the spent liquor processed from Quebracho and aluminum combination tanning trials have significantly reduced compared to the spent liquor of control Quebracho tanning trial.

Table-7: Characteristics of Spent Liquor for Experimental and Control

Experiment	COD (mg/l)	BOD_5 (mg/l)	TDS (mg/l)
Quebracho (control)	120900±3050	52000±1050	98200±1600
Al- Quebracho	108290±2100	35400±1400	76900±1100
Quebracho -Al	96950±1750	30200±1250	63800±1500

Chemical Analysis of the Crust Leather

The chemical analysis of crust leathers from control and experimental tanning trials are given in Table 8. The chemical analysis data for the experimental leathers is comparable to the control leathers.

Table-8: Chemical Analysis of crust leather of experimental and control

Parameter	Quebracho (control)	Al-Quebracho	Quebracho-Al
Moisture %	13.15	13.10	12.90
Total ash content %	2.75	2.40	2.40
Fats and oils %	3.45	3.30	2.90
Water soluble matter %	5.20	3.20	3.30
Hide substance %	52	53	52
Insoluble ash %	1.25	1.30	1.50
Degree of tannage %	47.98	49.25	52.69

CONCLUSIONS

The leather industry is suffering from the negative image generated by the pollution it causes to the environment. Combination tannage, like classic vegetable-aluminium tannage, is considered as suitable alternative for chrome-free tanning systems. .In the present study, an attempt has been made to produce upper leathers using a new eco-friendlier combination tanning process based on Quebracho and Aluminum. It is seen that combination tanning using Quebracho (20%) followed by Aluminum (2% Al_2O_3) resulted in leathers with shrinkage temperature of 104°C, which is 20°C more than the control (Quebracho tanned) leathers. Aluminum followed by Quebracho tanning resulted in leathers with shrinkage temperature 95°C. The physical and chemical characteristics of experimental leathers are comparable to control leathers. The experimental leathers are softer than the control leathers. The combination tanning using Quebracho and Aluminum appears to be an eco-friendlier option and results in leathers with good thermal stability and organoleptic properties that is important for commercial viability of the tanning system. This combination tanning contribute to the reduction of environmental impact

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