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Chestnut-Aluminium Combination tanning System for High Stability Leather

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Abstract— **Extensive research has been undertaken by many scientists in the modern leather industry and some alternative options have been proposed, among which the combination tanning of vegetable tannin and aluminum may be a good choice. In the present study, a combination tanning system based on Chestnut-Aluminum tannage for the production of upper leathers as a cleaner alternative is presented. The Castanea sativa powder (Chestnut) has been used in a combination tanning system based on Chestnut and Aluminum sulphate. Both tanning methodologies Chestnut followed by Aluminum (Chestnut-Al) and Aluminum followed by Chestnut (Al-Chestnut) have been attempted. Chestnut-Al leathers tanned using 20% Chestnut; followed by 2% Al2O3 resulted in shrinkage temperature of 100oC. However, Al-Chestnut leathers tanned using 2% Al2O3; followed by 20% Chestnut resulted in shrinkage temperature of 94oC. Chestnut-Al combination system resulted in leathers with good organoleptic and strength properties. The work presented in this paper established the use of Chestnut-aluminium combination tanning system as an effective alternative eco-friendly tanning process.**

Index Terms— **Aluminium sulphate, Chestnut, Combination tanning, leather, Castanea sativa.**

I. INTRODUCTION

Tanning involves a process that converts the putrescible hide and skin to resultant leather stabilized against heat, chemical corrosion, mechanical damage and microbiological degradations [1,2]. The most important materials in the leather making process are the tanning agents and different chemicals can be used to tan leather [3]. However, Chrome tanning, which was introduced in the latter half of the 19th century [4], is the most important tanning method for the leather industry and represents over 80% of the leather production world-wide [3,5,6] . Nevertheless, chromium is known as the main source of pollution due to the heavy metals resulted from the tanning wastewaters, wet finishing and mechanical processing of leathers [7-9]. Therefore, the growing environmental, health and safety concerns are forcing tanners to search and adopt alternative cleaner, safer, viable and benign tanning systems or change over to vegetable tanning again [5,6,10,11]. With the rising of eco-environmental awareness, chrome-free tanning as an eco-friendly technology has attracted increasing attention [12]. Nowadays, there is a globally growing requirement for chrome-free leather products, such as automotive leather, upholstery leather, upper leather and garment leather [13-15]. Besides, pastel shade leathers are popular in today's fashion world [16]. So far, there are many reports concerning the use of white minerals such as aluminum (III), zirconium (IV) and titanium (IV) salts, vegetable tannin [17], syntan [18], aldehydes and silica [19], to replace or reduce using conventional chrome tanning materials. Among them, vegetable tanning agent is considered as a promising alternative owing to its natural origin and appropriate tanning properties [20]. Nevertheless, it also faces several constraints like poor permeability, weak light fastness and difficulty in making pastel shades [21].

Vegetable tannins, polyphenolic compounds, are responsible for the tanning effects and being used in the stabilization of skin tracing back to the history of mankind [5,22]. These compounds are a complex and heterogeneous group of polyphenols widely distributed in plants with very diverse molecular weights ranging from 500 to 3,000 Da. Depending on the main polyphenolic constituent, tannins are divided into two main groups, condensed and hydrolysable tannins [23, 24]. The most common tannins presently used are extracted from chestnut wood, quebracho wood, tara pods, Chinese and Turkish gallnut, mimosa or wattle bark, oak wood, sumac leaves, and valonia oak acorn [23]. Rao and Nayudamma [25] 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 [26].

Castanea sativa Mill. belongs to the Fagaceae family and it is one of the most spread chestnut species [27]. The composition of tannins obtained from *Castanea sativa* wood [28], bark [29] and nut [30] has been determined and it was found that the main components belong to the group of hydrolysable tannins [31]. Based on their hydrolysis products, hydrolysable tannins include gallotannins and ellagitannins. In particular, sweet chestnut contains high amounts of ellagitannins (Fig.1), which form hexahydroxydiphenic (HHDP) acid (Fig.2). The

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name ellagitannins is derived from ellagic acid (Fig.3), which is created spontaneously in aqueous solution via an intra-molecular esterification reaction of HHDP acid [32]. The main ellagitannins found in *Castanea sativa* are castalin and vescalin [33], castalagin and vescalagin [34].

The tannins of wood are light in colour with little soluble non-tans and its Salt/Acid ratio is low enough. Chestnut is generally blended with other tannins like Wattle, Quebracho etc and used for the production of sole leather. In general chestnut tannin extract contain less salt and high percentage of acid. Bloom of ellagic acid is formed due to hydrolysis of tannin [35]. Sweetened chestnut is a normal extract chemically treated to improve its penetrating and firming qualities. Sweetened extract makes a yellow tannage whereas normal extract produces full, firm, water and wear resistant leather [36]. The aim of the present research work is to explore the possibilities of minimising the use of chrome. Since the chestnut contain a mixture of various polyphenolic compounds, an attempt has been made in this work to evaluate the combination tanning system with aluminium sulfate.

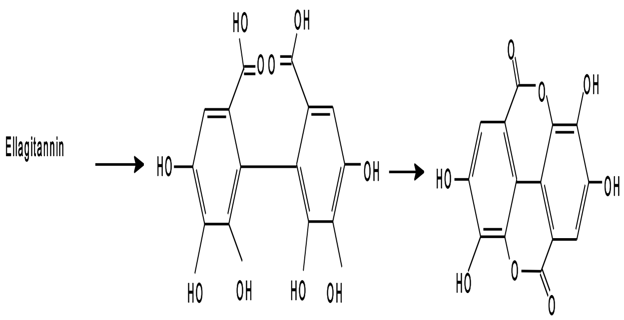

Figure 1. Hydrolysis of Ellagitannins (HHDP and Ellagic acid)

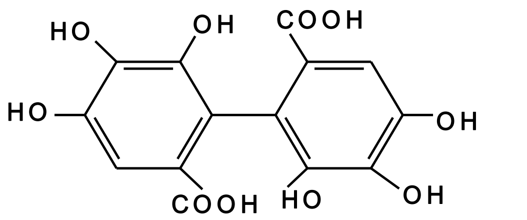

Figure 2. Hexahydroxydiphenic acid (HHDP)

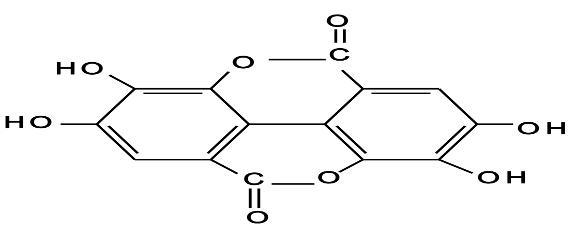

Figure 3. Ellagic acid

II. MATERIALS AND METHODS

Materials

Conventional processed pickled goat skins have been taken for tanning trials. Chestnut (*Castanea sativa*) and aluminum sulphate were used in tanning trials. Chemicals used for post tanning processes have been of commercial grade.

Preparation of 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

Chestnut -Al Sulphate Combination Tannage

Pickled goat skins have been used for combination tanning trials; Al-Chestnut tanning and Chestnut-Al tanning processes are given in Table I and II 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 Chestnut only as given in Table III. The post tanning process as mentioned in Table IV has been followed for experimental and control leathers.

Measurement of Hydrothermal Stability of Leathers

The most common method of measuring shrink temperature is to clamp the sample between two supports, immerse it in a heating medium (usually water or a glycerin-water mixture), and raise the temperature. At the shrink temperature the sample decreases in length. The shrinkage temperature of control and experimental leathers has been determined using Theis shrinkage tester [37]. 2X0.5 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.

Table I
Formulation of the Experimental Chestnut–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	Chestnut	120	
	10	Chestnut	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.

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.

Table II
Formulation of Experimental Aluminum- Chestnut 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_2O_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	Chestnut	90	
	10	Chestnut	90 ×	
Fixing	0.5	Formic acid	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.

Physical Testing

Samples for various physical tests from experimental and control crust leathers have been obtained as per IULTCS methods [38].Specimens have been 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 [39], grain crack strength [40] and tear strength [41] 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 Liquor

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 [42].

Chemical Analysis

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 [43] .Analyses were carried out in triplicates for each sample and the average values are reported.

III. RESULTS AND DISCUSSION

Combination tanning trials using Chestnut and Aluminum sulphate were carried out with Al_2O_3 at a concentration of 2% and 20% offer of Chestnut. The shrinkage temperature data of leathers tanned with Chestnut–Al and Al-Chestnut combination along with Chestnut control is given in Table V**.** From the table it is seen that both the combinations resulted in leathers with better shrinkage temperature than control leathers (Chestnut tanned). The shrinkage temperature of leathers obtained from Chestnut-Al combination tanning is higher than Al-Chestnut. However the combination tanning resulted in leathers with shrinkage temperature of 100°C, which is much better than control Chestnut leather of Ts 82°C. From Table V, it can be observed that Chestnut-Al combination tanning system resulted in enhancement of shrinkage temperature.

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. 4. Higher numbers indicate better property. From the figure, it is observed that Chestnut-Al combination tanned experimental crust leathers exhibited good fullness compared to Chestnut control leathers. The organoleptic properties of the Chestnut-Al crust leathers are better compared to Al-Chestnut crust leathers. This is primarily due to improved penetration and fixation of Chestnut in the experimental process, compared to control process.

Table III
Formulation of Control Chestnut Tanning Process for Goat Pickled Skin

Process	% *	Product	Duration (min)	Remarks
Adjustment of the pH	100	Water		
	0.75	Sodium bicarbonate	3 X 15	pH 4.5 -4.7
Tanning	2	Phenolic syntan	30	
	10	Chestnut	120	
	10	Chestnut	120	
Fixing	0.25	Formic acid	3X 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

Other properties such as softness, grain tightness, smoothness, dye uniformity and general appearance are comparable to that of conventionally processed leathers. The overall appearance of optimized experimental leathers is better than that of control and other experimental leathers.

Table IV
Formulation of Post-tanning Process for Control and Experimental 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

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

Table V
Shrinkage temperature of control and experimental tanning processes

Experiment	Shrinkage temperature (^oC)
Al-Chestnut (2% Al_2O_3)	94±1
Chestnut-Al (2% Al_2O_3)	100±1
Chestnut (Control)	82±1

Physical Testing of Experimental and Control Crust Leathers
It is very important to determine the effect the tanning process on the strength characteristics of leathers. 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 VI. It is observed that the tensile strength characteristics like tensile strength, elongation, tear strength of Chestnut-Al tanned crust leathers is found to be higher compared to that of the control and Al-Chestnut tanned crust leathers, whereas load at grain crack and distension at grain crack of both control and Al-Chestnut tanned leathers are found to be marginally lower.

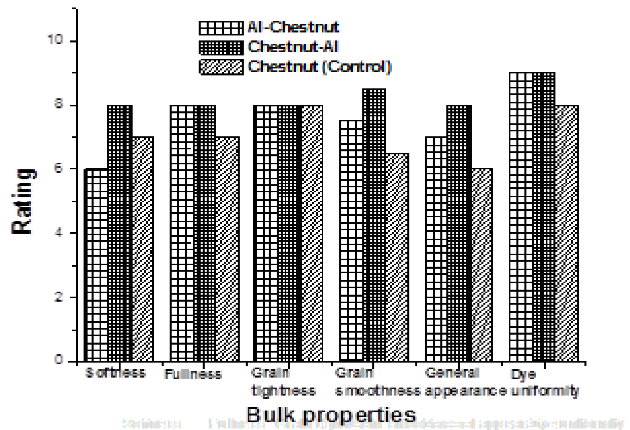

Figure 4: Graphical Representation of Organoleptic Properties of the Experimental and Control leather

Spent Liquor Analysis
Ecological concerns have become key issues in world industrial activities; in this context the eco-friendly combination tanning system is appropriate for a sustainable leather industry. The COD, BOD_5, and TDS of the spent liquor for experimental and control trials have been determined and are given in Table VII. 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 chestnut tanning (control). The BOD_5 and TDS of the spent liquor processed from chestnut and aluminum combination tanning trials have significantly reduced compared to the spent liquor of control chestnut tanning trial.

Chemical Analysis of the Crust Leather
The chemical analysis of crust leathers from control and experimental tanning trials are given in Table VIII. The chemical analysis data for the experimental leathers is comparable to the control leathers.

Table VI
Physical Strength Characteristics of Experimental and Control Crust Upper Leathers

Parameter	Al-Chestnut	Chestnut-Al	Control (Chestnut)	BIS Norms 44 (BIS 1992)
Tensile strength (Kg/cm^2)	225±3	245±2	215±3	200
Elongation at break (%)	46 ±0.60	59±0.60	43±0.70	40-65
Tear strength (Kg/cm)	40±0.65	46±0.65	38±0.65	30
Load at grain crack (Kg)	23±0.75	24±0.75	22±0.75	20
Distention at grain crack (mm)	10±0.60	11±0.60	10±0.60	7

IV. CONCLUSIONS

The combination tannage, like classic vegetable-aluminum combination tannage, is an very effective approach to achieve complementary characteristics .In the present study, an attempt has been made to produce upper leathers using a new eco-friendlier combination tanning process based on Chestnut and Aluminum. It is seen that combination tanning using Chestnut (20%) followed by Aluminum (2% Al_2O_3) resulted in leathers with shrinkage temperature of 100^oC, which is 18^oC more than the control (Chestnut tanned) leathers. Aluminum followed by Chestnut tanning resulted in leathers with shrinkage temperature 94^oC. 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 Chestnut 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.

Table VII
Characteristics of Spent Liquor for Experimental and Control

Experiment	COD (mg/l)	% reduction in COD	BOD_5 (mg/l)	% reduction in BOD	TDS (mg/l)	% reduction in TDS
Chestnut (control)	130800 ±3060	-	54500 ±1550	-	86800± 1500	-
Al-Chestnut	113790 ±2000	13	35040 ±1500	35.71	68550± 1200	21
Chestnut-Al	102550 ±1900	21.6	31350 ±1200	42.48	59100± 1400	32

Table VIII
Chemical Analysis of crust leather of experimental and control

Parameter	Chestnut (control)	Al-Chestnut	Chestnut-Al
Moisture %	13.45	13.20	12.70
Total ash content %	2.65	2.30	2.40
Fats and oils %	3.50	3.25	2.85
Water soluble matter %	4.90	3.10	3.35
Hide substance %	53	52	52
Insoluble ash %	1.30	1.45	1.55
Degree of tannage %	45	51.92	52.98

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