Application of Vegetable Bark Extract as Alternative Retanning Agent for Leather Processing

A.E Musa[1]*, G.A. Gasmelseed[2], E.F. Faki[3], H.E Ibrahim[2], O.A Haythem[4], M.A Manal[1], S.B Haythem[1]

1Department of Leather Technology, College of Applied and Industrial Sciences, University of Bahri, Khartoum – Sudan, P.O.Box 1660

2University of Science and Technology, Faculty of Engineering, Department of chemical engineering

Khartoum – Sudan

3Department of Leather Engineering, School of Industrial Engineering and Technology, Sudan University of Science and Technology, Khartoum – Sudan,

4National Leather Technology Centre, , Khartoum – Sudan

** Corresponding author: A.E Musa – musaalileather@gmail.com*

Abstract. The retanning process is considered as one of the most important processes in leather making, and it plays an important role in the modern leather industry. The fibre structure of hide or skin is not uniform and the retanning agent improves the properties of leather by filling the empty part of wet-blue leather. It could contribute to further stabilization of collagen fibres and give better handle properties to leather such as fullness and elasticity. In a conventional leather retanning process, retanning materials used include both inorganic salt like basic chromium salt, zirconium salt and aluminum salt and organic materials such as vegetable tanning agent, synthetic tanning agent, resin retanning and aldehyde tanning agent. Extract from the barks of Acacia seyal (Talh bark), widely distributed in Sudan, has been evaluated for its utilization in the retanning of the leather and presented in this paper. Barks of talh have been extracted for 1 hour with distilled water (1:10 w/v) at temperature above 80˚C. The talh extract prepared has been used for the retanning of wet blue leathers. The effectiveness of talh extract in retanning of wet blue leathers has been compared with mimosa retanning. The organoleptic properties of the leathers viz. softness, fullness, grain smoothness, grain tightness (break), general appearance, uniformity of dyeing of talh retanned leather have been evaluated in comparison with mimosa retanned leathers. Talh retanning resulted in leathers with good grain tightness. Dyeing characteristics of talh retanned leathers have been found to be better than mimosa retanned leathers. Also physical strength characteristic and shrinkage temperature and economic viability were noted. The effluent arising from this retanning system has been analyzed for its environmental impact.

1. Introduction

Retanning process plays an important role in leather making because it can improve the cutting value, the handle and some specific properties of leathers (like buffing property, embossing property, perspiration resistance, fastness to washing, flammability, etc.) by using various types of retanning agents and modifying their application processes[1-4]. The retanning performance depends on the penetration and the uptake of retanning agents in leather, which are mainly controlled by the electrostatic force between the retanning agent and the surface of the leather collagen fiber[5-7]. Therefore, in order to improve the retanning performance scientifically, it is essential to fully understand the surface charges of both retanning agents and leathers and their effect on the penetration and the uptake of retanning agents in leather during retanning process.

In order to meet customers' requirements, a wide variety of retanning agents is used in retanning process, such as mineral retanning agents[8], vegetable tannins[9], Syntans[10-12], resins[8,13], polymers[14,15] which could bring about a difference in adsorption capacity of leather to water and may influence the thermal stability closely related to the moisture content of leather[16].

Bio-active ingredients in the form of tannins are present in some of the plant materials capable of imparting tanning effect. The vegetable tannins are water-soluble polyphenolic compounds having molecular weight in the range of 500 –3000 Daltons[17, 18]. They occur in bark, wood, fruits, fruit pods, leaves, roots, and plant galls[19,20]. Based on their chemical structure, the vegetable tannins are classified as Hydrolysable type (e.g. Myrobalan) and Condensed type (e.g. Wattle).

Hydrolysable type tannins are based on esters of phenol carboxylic acid and glucose such as 1,2,3,4,6-pentagalloyl glucose (**Fig. 1**) along with several other compounds[21]. Condensed or flavonoid tannins being structurally related to flavonoid group of compounds, form insoluble "phlobaphenes" or tannins reds on the treatment on mineral acids in aqueous media[22]. The typical structure of flavanoid is shown in **Fig.2**. The condensed tannins, also called proanthocyanidins are oligomers and polymers formed in the flavan-3-ol basic structure ie . epicatechin and catechin (**Fig. 3**) [23].

The manufacture of the vegetable tanning extract is based on extraction of tannin using a suitable solvent, usually water, followed by concentration and spray drying (to get powder) or vacuum dried (to get solid) [18].

Sudan has various indigenous tanning materials. Some of these, such as Garad pods (*Acacia nilotica sub. sp. nilotica*) and Talh bark (*Acacia seyal*) are used extensively in the Sudan by rural tanners[24].

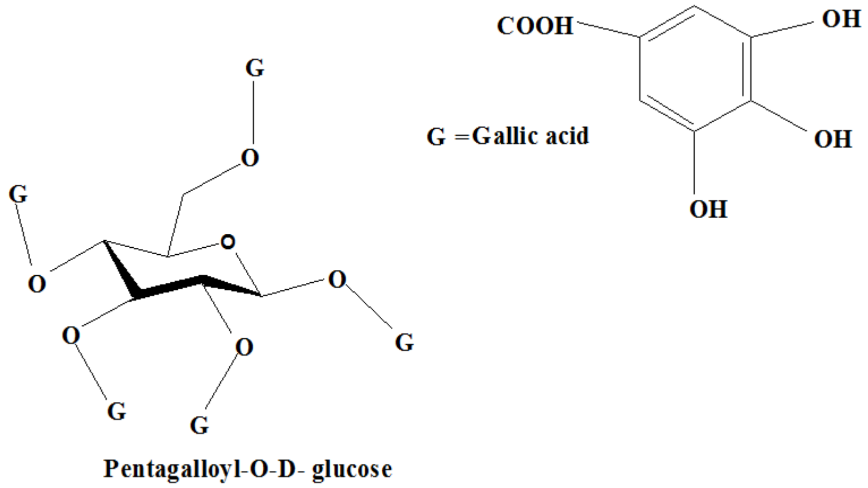

Fig. 1. 1,2,3,4,6-pentagalloyl glucose.

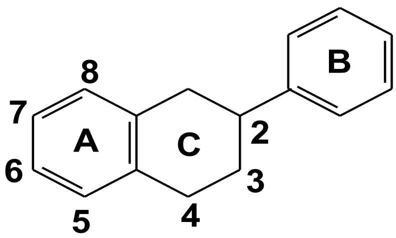

Fig. 2. Structure of flavonoids.

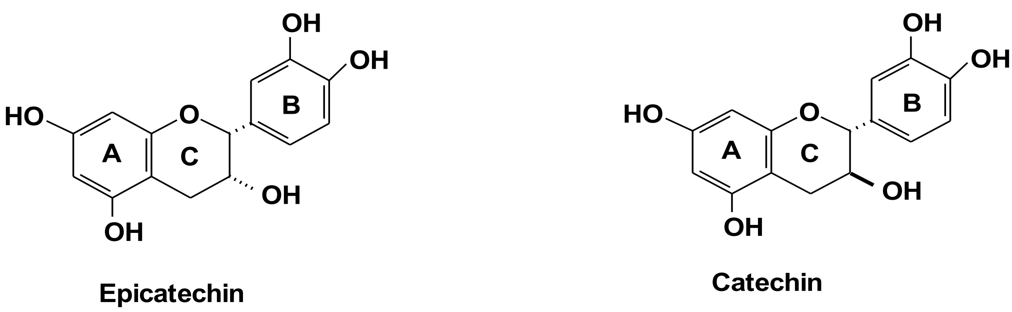

Fig. 3. Structure of epicatechin and catechin (Flavan-3-ols).

Acacia seyal pods and bark contain 20% tannin. The acacia seyal bark contains 18-30 % tannins and is a source of red dye. The bark, leaves and gums are used for colds, diarrhoea, hemorrhage, jaundice, headache and burns. A bark decoction is used against leprosy and dysentery, is a stimulant and acts as a purgative for humans and animals. Exposure to smoke is believed to relieve rheumatic pains[25]. Since the *acacia seyal* bark (Talh bark) extract contains polyphenolic compounds with varied molecular weight, an attempt has been made in this study to utilize them for the retanning of wet blue leathers to produce upper leathers.

2. Materials and Methods

2.1 Materials

Conventionally processed wet blue goat skins were taken for the tanning trials. Talh (*acacia seyal*) barks were sourced from Sudan. Chemicals used for post tanning were of commercial grade. Chemicals used for the analysis of spent liquor were of analytical reagent.

2.2 Aqueous Extraction of Talh Barks

The required amount of ground talh (*Acacia seyal*) barks were soaked in water (1:10 w/v) at temperature above 80°C in water bath for an hour, filtered through a piece of cotton cloth and the volume of the talh extract is noted. Part of the talh extract was filtered through Whatman no.1 filter paper and 10 ml of filtrate were used for the determination of percentage total solubles.

2.3 Retanning Trials

The retanning experiments were carried out on conventionally processed wet blue goat skins using talh barks extract. The retanning trials were carried out using mimosa as a matched pair control as a comparison for the experimental leathers. The post tanning process mentioned in Table 1 and Table 2 followed for both experimental and control leathers.

Table 1. Experimental Formulation of Post-tanning process for making upper crusts, Raw material: Shaved wet blue goat skins of thickness ~1.2 mm, % chemicals for post tanning process is based on shaved weight.

Process	%	Product	Duration (min)	Remarks
Washing	200	Water	10	Drain
Neutralization	100	water		
	1	Sodium formate		
	0.75	Sodium bicarbonate	3× 15	pH 5-5.5
Retanning	20	Talh barks extract	1 hour	
Fatliquoring	10	Synthеic fatliquor	90 min	
Dyeing	3	Acid brown dye	45 min	Penetration of dye was checked
Fixing	1.5	Formic acid	3 x 10 +30 min	pH 3.5
Washing	200	Water	10 min	Leathers were piled over night; Next day set, hooked to dry, staked, trimmed and buffed

2.4 Determination of Shrinkage Temperature

The shrinkage temperature of both control and experimental leathers were determined using the Theis shrinkage tester[26]. A 2cm sample, cut out from the leather was clamped between the jaws of the clamp, which in turn was immersed in a solution of glycerol: water mixture (3:1). The solution was stirred using mechanical stirrer attached with the shrinkage tester. The temperature of the solution was gradually increased and the temperature at which the sample shrinks was noted. Triplicates were carried out for each sample and the average values are reported.

Table 2. Control Formulation of Post-tanning process for making upper crusts, Raw material: Shaved wet blue goat skins of thickness ~1.2 mm, % chemicals for post tanning process is based on shaved weight.

Process	%	Product	Duration (min)	Remarks
Washing	200	Water	10	Drain
Neutralization	100	water		
	1	Sodium formate		
	0.75	Sodium bicarbonate	3× 15	pH 5-5.5
Retanning	20	Mimosa	1 hour	
Fatliquoring	10	Syntheic fatliquor	90 min	
Dyeing	3	Acid brown dye	45 min	Penetration of dye was checked
Fixing	1.5	Formic acid	3 x 10 +30 min	pH 3.5
Washing	200	Water	10 min	Leathers were piled over night; Next day set, hooked to dry, staked, trimmed and buffed

2.5 Evaluation of Organoleptic Properties

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. The tanners have also evaluated the dyeing characteristics viz., uniformity of dye, shade intensity and differential dyeing for both experimental and control crust leathers.

2.6 Mechanical Properties Test of Leather Samples

Samples for various physical tests from experimental and control crust leathers were obtained as per IULTCS methods[27]. Specimens were conditioned at 20 ± 2 °C and 65 ± 2 % R.H over a period of 48 hrs. Mechanical properties such as tensile strength, percentage elongation at break[28], grain crack strength[29] and tear strength[30] were measured as per standard procedures. Each value reported is an average of four (2 along the backbone, 2 across the back bone) samples.

2.7 Analysis of Composite Waste Liquor

The spent liquor from control and experimental post tanning processing were collected, filtered and analyzed for chemical oxygen demand (COD), Biochemical oxygen demand (BOD_5), and total solids (TS) as per standard procedures[31].

2.8 Chemical Analysis

The chemical analysis of the leathers viz. for % moisture, total ash content, % oils and fats, % water soluble, % insoluble ash % hide substance, and degree of tannage were carried out for control and experimental leathers as per standard procedures[32] Triplicates were carried out for each sample and the average values are reported.

3. Results and Discussion

3.1 Shrinkage Temperature

The way to determine that the tanning process has been carried correctly is to measure the 'hydrothermal stability' – its resistance to wet heat – more commonly referred to as the 'shrinkage temperature'. A characteristic of hides, skins and leathers is that if they are gradually heated in water, they reach a temperature at which they are subject to sudden, irreversible shrinkage. The shrinkage temperature of wet blue leathers retanned using talh and wattle is given in Table 3. The wet blue leathers resulted in shrinkage temperature of 109˚C; however the retanning with wattle and talh resulted in increase of shrinkage temperature to 117˚C and 113˚C respectively. It is clear that the treatment of talh enhances the shrinkage temperature significantly similar to the case of wattle; hence retanning with talh bark extract improved the hydrothermal stability.

Table 3. Shrinkage temperature of crust leathers retanned with talh and wattle.

Sample	Shrinkage temperature, Ts (°C)
Wattle (Control)	117±3
Talh (Experimental)	113±2

Note- Shrinkage temperature of wet blue leathers were 109±2˚C

3.2 Organoleptic Properties Assessed by Tactile Evaluation

The organoleptic properties of leathers retanned using talh and control wattle is given in **Fig. 4**. Higher numbers indicate better property. From the figure it is observed that retanning with talh resulted in leathers with good grain tightness and roundness compared to wattle retanned leathers. The fullness of the leathers with talh retanning had been found to be comparable to that of wattle. However, the softness of leathers with wattle retanning is found to be better than that of talh. To be an effective agent for retanning, the retanning material should improve the fullness, grain tightness and roundness of the leather, as they are the important parameters especially for making upper leathers. The grain smoothness of talh retanned leathers has been found to be similar to that of wattle retanning. On the whole the leathers retanned with talh had been found to be better than wattle retannng. Hence using talh bark extract appears to be a good alternative for the retanning processes for making leathers with good organoleptic properties.

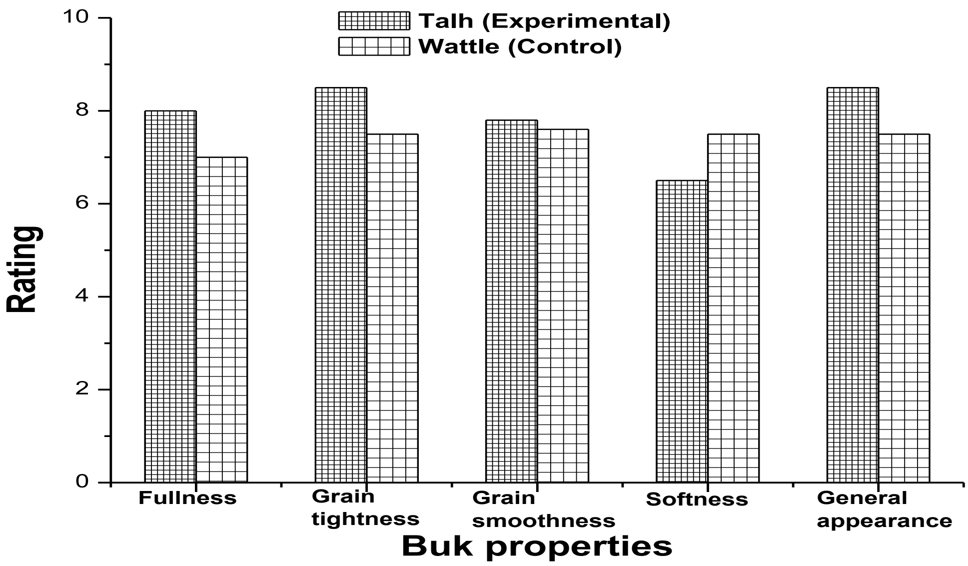

Fig. 4. Graphical representation of organoleptic properties of the experimental and control crust leathers.

3.3 Dyeing Characteristics of Talh Retanned Leathers

The dyeing characteristics of talh and wattle retanned leathers have been evaluated by experienced tanners and the results are given in Table 4. The uniformity of dye of the talh retanned leathers has been found to be similar to wattle retanned leathers. The shade intensity of the talh retanned leathers has been found to be better than the wattle retanned leathers. No differential dyeing (between grain and flesh) has been observed for both talh and wattle retanned leathers. The overall performance of both control and experimental leathers are comparable.

Table 4. Visual evaluation of the dyeing characteristics of crust leathers retanned with talh a and wattle.

Property	Talh (Experimental)	Wattle (Control)
Uniformity of dye	Good	Good
Shade intensity	V.good	Good
Differential Dyeing	Nil	Nil

3.4 Mechanical Properties of Talh Retanned Leathers

The physical strength measurements of matched pair talh retanned experimental and wattle retanned control leathers are given in Table 5. The physical strength measurements viz., tensile strength, elongation, tear strength, load at grain crack and distension at grain has been found to be comparable. The strength values of talh retanned leathers have been found to meet the BIS standards[33] for chrome retanned leathers.

Table 5. Physical strength characteristics of crust leather retanned using talh (Exp) and wattle (Con.).

Property	Talh	Wattle	BIS norms*
Tensile strength (Kg/cm^2)	255± 5	252±5	250
Elongation at break (%)	67± 2	65±2	60-70
Tear strength (Kg/cm thickness)	48±2	46±2	30
Load at grain crack (kg)	26±3	24±5	20
Distention at grain crack (mm)	10.5±0.5	9.4±0.2	Min 7

* Bureau of Indian standards (BIS) specification for chrome retanned upper leathers

3.5 Environmental benefits

Oxygen demand, biological oxygen demand and total solids are main parameters in assessing the quality of wastewater. The COD, BOD_5 and TS of the spent liquor for both experimental and control trials were determined and are given in Table 6. From the table it is observed that the COD and BOD of the spent liquor processed using talh retanning is lesser than the spent liquor from wattle retanning. However the environmental impact of talh retan liquor has been observed to be lesser than the wattle retan liquor.

Table 6. Characteristic of spent liquor for control and experimental post tanning trials.

Parameter	Talh (Experimental)	Wattle (Control)
COD (mg/l)	81600±1200	93500±2550
BOD_5 (mg/l)	32800±900	34500±800
Total solid (mg/l)	23560±740	32650±750

3.6 Chemical Analysis of the crust leather

The chemical measurements of matched pair experimental crust leather (talh) and control (Wattle) are given in Table 7. The chemical analysis data for the experimental leathers is comparable to the control leathers. However, the water soluble matter for the control (wattle) leathers is more than the experimental leathers (talh).

Table 7. Chemical Analysis of crust leather of experimental and control.

Parameter	Talh (experimental)	Wattle (control)
Moisture (%)	13.10	12.30
Total ash content (%)	3.00	2.70
Fats and oils (%)	3.60	3.30
Water soluble matter (%)	5.40	4.70
Insoluble ash (%)	1.30	1.10
Hide substance (%)	50	51
Degree of tannage (%)	53	54.12

4. Conclusions

Retanning plays an important role in the leather industry. It can not only further supplement tanning, improve the fullness and softness of leather, tighten the grain of leather, but also can enhance the hydrothermal stability, level-dyeing property and wear resistance of leather. Meanwhile, the retanning process is helpful to subsequent finishing operations. Therefore, the quality of the retanning materials is a significant factor to determine the effect of retanning. Most organoleptic properties of the experimental leathers produced from talh bark extract are better than control leathers produced from wattle. However softness property is better in the case of wattle retanned leather and the mechanical properties are comparable with the matched pair control leathers. Retanning with talh also enhances in intense dyeing. Hence using talh bark extract appears to be a good alternative for the retanning processes viz., it can complement the tanning effect, improving fullness and softness of the leather plus, having a certain of filling performance especially in the looser parts such as the belly, and make a firmer grain and fuller leather. In addition, there is a certain enhancement for the hydrothermal stability and dyeing uniformity.

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