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RESEARCH ARTICLE 25

Haraz Bark Powder Extract for Manufacture of Nappa Upper Leather as Alternative Retanning Agent

S.B Ali[1], H.E Haroun[2] and A.E Musa*[3]

(1)Department of Leather Engineering, College of Engineering, Sudan University of Science and Technology, Khartoum – Sudan,
Telephone: +249912831874

(2)Department of Leather Engineering, College of Engineering, Sudan University of Science and Technology, Khartoum – Sudan,
Telephone: +249122564532

*(3)Department of Leather Technology, College of Applied and Industrial Sciences, University of Bahri, Khartoum – Sudan, P.O.Box 12327
Telephone: +249919440560

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***Abstract*— The retannage process achieves a wide variety of purposes and is applicable to different kinds of chrome leather. The objectives of the process, to fill the looser and softer parts of leather in order to produce leathers of more uniform physical properties, to allow for the production of unlined footwear, to improve the chemical stability of the leather and to allow rapid finishing and delivery to the customer. Extract from the barks of *Faidherbia albida* (haraz), widely distributed in Sudan, and has been evaluated for its utilization in the retanning of the leather and presented in this paper. Barks of haraz have been extracted for 1 hour with distilled water (1:10 w/v) at temperature above 80˚C. The haraz extract prepared has been used for the retanning of wet blue leathers. The effectiveness of haraz extract in retanning of wet blue leathers has been compared with wattle retanning. The organoleptic properties of the leathers viz. softness, fullness, grain smoothness, grain tightness (break), general appearance, uniformity of dyeing of haraz retanned leather have been evaluated in comparison with wattle retanned leathers. Haraz retanning resulted in leathers with good grain tightness. Dyeing characteristics of haraz retanned leathers have been found to be better than wattle retanned leathers. Also physical strength characteristic and shrinkage temperature and were noted**

***Index Terms*— Retannage; Haraz; Chrome leather, Nappa leather**

I. INTRODUCTION

The term 'post tanning' refer to the wet processing steps that follow the primary tanning reaction. This might refer to following tannage with chromium (III), as usually the case in industry, but equally it applies to vegetable tanning or indeed any other tannage used to confer the primary stabilization to pelt. In all cases, post tanning can be separated into three generic processes: retanning, dyeing and fatliquoring [1]. Retanning may be a single chemical process or may be a combination of reactions applied together or more usually consecutively. The purpose is to modify the properties and performance of the leather. These changes include the handle, the chemical and hydrothermal stability or the appearance of the leather. The effects are dependent on both the primary tanning chemistry and the retanning reactions [1].

Vegetable tannins materials are widely employed for retanning side leather and they are occasionally used in calf and goatskin in upper leather productions. They are also widely employed as general mordants for the production of dry crust tanned chrome leathers. They are cheap, readily, good filling agents, and make the grain hydrophilic. The condensed tannins, such as mimosa or quebracho, reduce the chrome characteristics only very slightly but give leathers of poor fastness. The most widely condensed tannins are based on (-)- epicatechin(**Fig. 1)** and (+) - catechin (**Fig. 2**) [2]. The hydrolzable tannins, such as sumach, myrabolans, or chestnut, give leathers of improved light fastness and soft mellow handle [3]. Hydrolysable tannins containing gallic acid (**Fig. 3**) esterified with glucose [2].

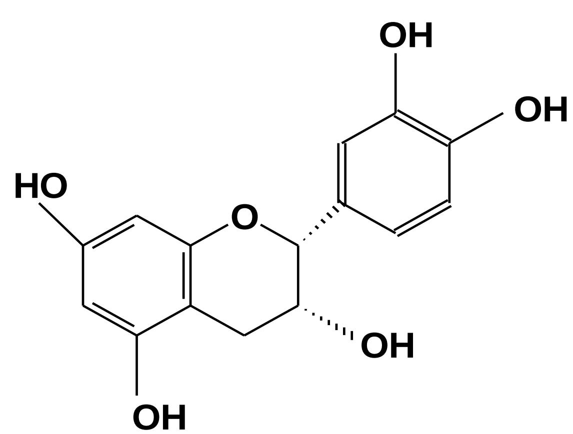

Figure 1. Epicatechin

*Corresponding author E-mail: ali206w@hotmail.com

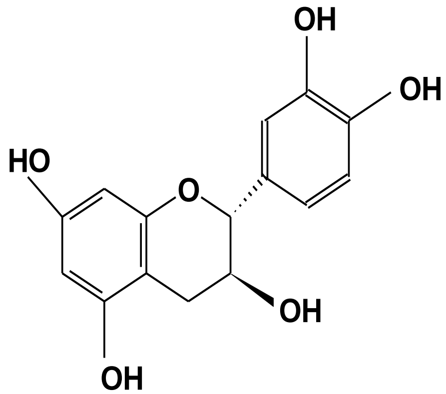

Figure 2. Catechin

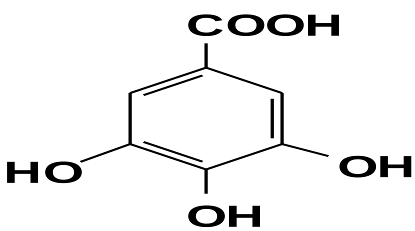

Figure 3. Gallic acid

In Sudan, *Faidherbia albida* is most common on silty loams with sufficient subsoil moisture, e.g., along rivers. It is found in most parts of Sudan but its best development is in the western part of the country, particularly in the Jebel Marra area. The tree does not grow on iron soils or waterlogged sites. *Acacia nilotica* and *A. seyal* can be found mixed with *F. albida* in Sudan [4]. The bark is reported to contain as much as 28% tannin that of the main trunk and is used for treating hides. *Faidherbia albida* **(**haraz**)** is a member of the legume family and of the subfamily *Mimosoideae*. The species is characterized by bipinnate leaves, orange curled seed pods, cream colored flowers, and thorns.[5, 6].

Up to now, leather tanning is dominated by the use of chromium (III) salts, because it gives leather unmatchable hydrothermal stability and excellent organoleptic properties [7]. However, chrome tanning has some negative attributes, posing serious challenges to our continued reliance on it. As a limited resource, chromium (VI) is a well-known carcinogen, but chromium (III) is considered as non-toxic [8]. The chromium (III) existing in leather might be transformed into chromium (VI) in some extreme conditions [9]. Therefore, the chrome remaining in wastewater and the solid wastes may be harmful to the environment. The disposal of these wastes brings many difficulties for the leather industries in complying with the emerging regulations [10]. In fact, some countries have restricted the use of chrome-tanned leather for certain purposes [11]. An effective alternative for chromium must be; abundant in nature, easily obtained; low price; environmental-friendly and should offer a competitive performance to that of chrome-tanned leather. In addition, it must be both easy and safe to use [12]. Three-dimensional interweaving of collagen fibre bundles is responsible for its characteristic mechanical properties which are important characteristics of sheep nappa leathers and influence their end use and comfort. Construction of garments from leather involves techniques that are similar to those used for garments made from woven fabrics. However, leather differs from textiles primarily because of the nature of the interwoven three dimensional collagen networks. There are numerous pores both in the fibrous network and between collagen molecules, which may give leathers with good air/vapour permeability [13]. Since the haraz extract contains mixture of several compounds with varied molecular weight including polyphenols, an attempt has been made in this study to utilize them for the retanning of wet blue leathers to produce nappa upper leather.

II. MATERIALS AND METHODS

Materials

Conventionally processed wet blue goat skins were taken for the re-tanning trials. *Haraz* (*Faidherbia albida*) barks were sourced from Sudan. Chemicals used for post tanning were of commercial grade.

Aqueous Extraction of Haraz barks

The required amount of ground haraz (*Faidherbia albida*) barks were soaked in water (1:10 w/v) at temperature above 80^{o}C in water bath for an hour, filtered through the piece of cotton cloth and then concentrated to certain volume and used in re-tanning.

Retanning Trials

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

Determination of shrinkage temperature

The shrinkage temperature of both control and experimental leathers were determined using the Theis shrinkage tester [14]. 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.

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

Physical testing

Samples for various physical tests from experimental and control crust leathers were obtained as per IULTCS methods [15]. Specimens were 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, [16] grain crack strength [17] and tear strength [18] were measured as per standard procedures. Each value reported is an average of four (2 along the backbone, 2 across the back bone) samples.

Chemical Analysis

The chemical analysis of the leathers viz. for % moisture, total ash content, % oils and fats, % water soluble, and % insoluble ash were carried out for control and experimental leathers as per standard procedures [19] Triplicates were carried out for each sample and the average values are reported.

Table 1

Formulation of Post-tanning process for making upper crusts
Raw material: Shaved wet blue goat skins of thickness ~1.0 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	Haraz (Experimental)/ Wattle (Control)	1 hour	
Fatliquoring	5	Lipoderm liquor SAF (Syntheic fatliquor)	45 min	
Dyeing	3	Acid brown dye	45 min	Penetration of dye was checked
Fatliquoring	5	Lipoderm liquor SAF (Syntheic fatliquor)	45 min	
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

III. RESULTS AND DISCUSSION

Shrinkage temperature

Shrinkage temperature (referred to as Ts) is one of the most important parameters in characterizing the thermal stability of leather. It is the temperature at which the leather sample starts to shrink in water or other heating medium. Rapid and accurate determination of Ts is of great significance for the industrial leather production process as well as professionals in-depth research. The shrinkage temperature of wet blue crust leathers retanned using haraz and wattle is given in **Table 2**. The wet blue leathers resulted in shrinkage temperature of 109˚C; however the retanning with wattle and haraz resulted in increase of shrinkage temperature to 114˚C and 112˚C respectively. It is clear that the treatment of haraz enhances the shrinkage temperature significantly similar to the case of wattle; hence retanning with haraz appears to be a promising option in terms of its reactivity with the leather matrix.

Table 2
Shrinkage temperature of crust leathers retanned with haraz and wattle

Sample	Shrinkage temperature, Ts (°C)
Wattle (Control)	114±3
Haraz (Experimental)	112±2

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

Organoleptic properties of haraz retanned leathers

The organoleptic properties of leathers retanned using haraz and control wattle is given in **Table 3**. From the table it is observed that retanning with haraz resulted in leathers with good grain tightness and roundness compared to wattle retanned leathers. The fullness of the leathers with haraz 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 haraz. 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 haraz retanned leathers has been found to be similar to that of wattle retanning. On the whole the leathers retanned with haraz had been found to be better than wattle retannng. Hence use of haraz for retanning appears to be a fruitful option for making leathers with good organoleptic properties.

Table 3
Organoleptic properties of crust leathers retanned with haraz and wattle

Property	Haraz (Experimental)	Wattle (Control)
Fullness	8±1	7.40±1
Grain tightness	8.6±0.4	6.8±0.3
Grain smoothness	7.8±0.4	7.6±0.4
Softness	6.5±0.2	7.5±0
General appearance	8.4±0.5	7.7±0.4

Dyeing Characteristics of haraz Retanned Leathers

The dyeing characteristics of haraz and wattle retanned leathers have been evaluated by experienced tanners and the results are given in **Table 4**. The uniformity of dye of the haraz retanned leathers has been found to be better than the wattle retanned leathers. The shade intensity of the haraz 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 haraz and wattle retanned leathers. It is clear that the use of haraz did not affect the dyeing characteristics of the leather compared to control; rather it enhances uniformity of dye and the shade intensity of the leathers, which is benevolent in obtaining leathers with brilliant shades.

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

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

Physical strength characteristics of haraz retanned leathers

The physical strength measurements of matched pair haraz 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 haraz retanned leathers have been found to meet the BIS standards [20] for chrome retanned leathers.

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

Property	Haraz	Wattle	BIS norms*
Tensile strength (Kg/cm2)	255.15±16.7	251±20.8	250
Elongation at break (%)	67. 16± 9.42	65. 48 ±3.80	60-70
Tear strength (Kg/cm thickness)	42.92±7.56	43.43±3.56	30
Load at grain crack (kg)	25±4	23±5	20
Distention at grain crack (mm)	10.22±0.74	9.46±0.42	Min 7

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

Chemical Analysis of the crust leather

The chemical measurements of matched pair experimental crust leather (haraz) and control (Wattle) are given in **Table 6**. 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 (haraz).

Table 6
Chemical Analysis of crust leather of experimental and control

Parameter	Haraz (experimental)	Wattle (control)
Moisture %	12.20	15.30
Total ash content %	3	3.2
Fats and oils %	6.20	6
Water soluble matter %	5.8	6.2
Insoluble ash %	1.60	1.45

IV. CONCLUSIONS

The retanning may be a single chemical process or may be a combination of reactions applied together or more usually consecutively. The purpose is to modify the properties and performance of the leather. These changes include the handle, the chemical and hydrothermal stability or the appearance of the leather. The effects are dependent on both the primary tanning chemistry and the retanning reactions. Most organoleptic properties of the experimental leathers produced from haraz bark extract are better than control leathers produced from wattle. However softness property is better in the case of wattle retanned leather and the physical strength properties are comparable with the matched pair control leathers. Retanning with haraz also facilitates in intense dyeing. Hence using haraz appears to be a good alternative for the retanning processes. Further exploration is required to find effective utilization of haraz extract in leather processing.

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