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Research Article

Sunt Bark Powder: Alternative Retanning Agent for Shoe Upper Leather Manufacture

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Abstract

The retanning process is a very important step in leather manufacturing because it overcomes some of the disadvantages of chrome tannage and it can contributes to further stabilization of collagen fibers and good handle of leather, such as fullness, softness, elasticity and so on. In order to meet customers' requirements, a wide variety of retanning agents are used in retanning process viz. vegetable tan and phenolic synthetic/organic tanning materials. Sunt bark, widely distributed in Sudan, has been evaluated for its utilization in the retanning of the leathers. In the present investigation, sunt bark powder has been used for the retanning of wet blue leathers. The effectiveness sunt bark 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 sunt bark retanned leather have been evaluated in comparison with wattle retanned leathers. Sunt retanning resulted in leathers with good grain tightness. Physical strength characteristic and shrinkage temperature were noted. Dyeing characteristics of sunt retanned leathers have been found to be better than wattle retanned leathers.

Keywords: *Sunt bark, Retanning, Garad bark, Acacia nilotica, Shoe upper leather*

1. Introduction

Many plant materials contain polyphenols which can be used in tanning. To be effective, the molecular mass must be in the range 500 –3000; lower molecular mass fractions in the tannin are referred to as non-tans and higher molecular mass species are gums, which are sugar complexes with polyphenols (Covington, 2006).
Vegetable tannins are polyphenolic biopolymers and are secondary metabolites widely distributed in the various sectors of the higher plant kingdom (Bickley, 1992; Hua and Haslam, 1995). All vegetable tannins are derivatives of phenol (Fig. 1).

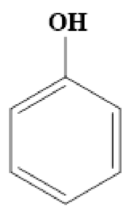

Figure 1: Phenol

A phenolic hydroxy group is much more acidic than an alcoholic one. Vegetable tannins contain benzene rings which bear not one, but several hydroxy groups. The compounds: catechol (Fig. 2), pyrogallol (Fig. 3) and gallic acid (Fig. 4) are examples of some simple polyhydric phenols (Reed 1969).

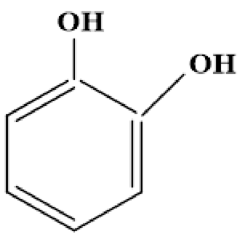

Figure 2: Catechol

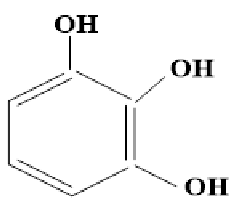

Figure 3: Pyrogallol

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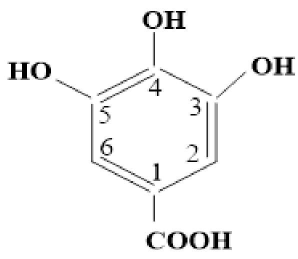

Figure 4: Gallic acid

Tannins traditionally are used in the production of leather (Tang et al., 1996). However; other industries are finding tannins useful. In the oil industry vegetable tannins are used as additives in drilling fluids. The food industry uses tannins to add flavor, taste, color and nutritional value to foods (Hemingway and Karchesy, 1992; Pazmino et al., 2001). Adhesives based on reaction of tannins and formaldehyde are also being formulated. In addition, polyphenols have formed major constituents of a lot of pharmaceuticals of natural herbal medicines (Papoutsi et al., 2005). Tannins as antioxidants are very useful in physiological processes (Shan et al., 2005). The antioxidative effect is due to their redox properties, which emanate from their free radical scavenging activity, transition metal chelating activity, and singlet-oxygen- quenching capacity (Rice et al., 1997; Chen and Ahn , 1998; Luiz et al., 2002).The vegetable tanning agents used for processing of different types of leathers are leached from woods of trees like quebracho and chestnut extract, fruits and fruits pods, leaves, roots etc., which are water soluble, noncrystalline ingredients of plant matter. The vegetable tannins possess distinct astringency. Chemically, tannins are mixture of several molecular species (Okuda et al., 1995). There are two types of vegetable tannins: hydrolysable tannins (gallotannins and ellagitannins) and condensed tannins.

Retanning is one of the essential steps in leather processing. It follows the primary tanning process, utilising synthetic tanning agents (syntans) to impart certain functional properties to the final leather, including hygienic properties (Nashy et al., 2012). Retannage is a process used to improve roundness, grain firmness and leather filling by the use of vegetable tannins, syntans and various types of resins (Bragancai et al., 2013). The most desirable target of retannage was always to level out the structure of a skin or hide by filling the loose and empty parts in the bellies and necks to improve the cutting value (Hubert and Wachsmann 1999).

To the rural tanner of tropical and subtropical Africa and Asia, the acacias are one of the most important tannin-bearing trees. Several species, such as *Acacia Arabica*, *A. nilotica* and *A.adamsonia*, have supplied pods and bark since immemorial times. They probably explain the origins of vegetable tanning in Africa and Asia. The leather produced by acacia pods is soft, plump, light colored and durable, and it can be readily dyed. Their solutions are mellow. No wonder highly skilled artists appeared in those countries where the acacia is grown. The acacia pods and bark are known variously in the countries where they grow as babul (hindustan), babar (Sind) garad or sunt (Sudan), neb neb (*West Africa*) and gabarua (Nigeria) (FAO, 1960).The pods used for tanning are from 10 to 15 centrimeters long and 1 centimeter broad, and they have 8 to 10 seeds. Contrary to common belief, the seeds do not contain tannin, which is present only in the pods. The pods should be collected when they are ripe: for their tannin-content reaches the highest level just as they are falling from the trees; it is inadvisable to wait to collect the pods from the ground, for they will then be contaminated with sand, clay, moulds and other undesirable matter. According to the conditions of the soil and the climate, their tannin-content varies from 20 to 30%. The material contains an undue proportion of nontans and a high proportion of sugary matter in the seeds. This results in a rapid fermentation of the liquor. The bark of the *Acacia Arabica* does not contain more than 14% tannin and is mostly used in northern India under the name of babul bark. The bark from old trees yields a very dark colored tannin. It is best, therefore, to strip from trees which are from five to seven years old. When babul bark is used for tanning, it gives a leather which has a darker color and a tendency to crack and tear; but when it is suitably blended with myrobalan (3:1) or with a varam bark, it can be used with advantage, particularly in sole leather tannage (FAO, 1960). *Acacia nilotica* (Sunt in Arabic) is a member family of subfamily *Mimosoidae* of leguminous trees. It is of multiple uses in the Sudan, Africa and many Arabic countries. The tree is readily distinguished by the long white spines, yellow head inflorescene and the grey necklace-like pods. Three subspecies are commonly found in the Sudan, namely *tomentosa* that characterized by the pubescent pods and grow throughout Sudan, *nilotica* that characterized by the glabrous pods and grow along the White Nile and *adansonii* that characterized by the broad pods and grow in western Sudan (Kamal et al., 2005). The current investigation aimed to utilize sunt (garad) bark powder for the retanning of wet blue leathers to produce *shoe upper leather* since the sunt (garad) bark powder contains mixture of several compounds with varied molecular weight including polyphenols.

2. Materials and Methods

Materials

Conventionally processed wet blue goat skins were taken for the re-tanning trials. Sunt (*Acacia nilotica*) barks were sourced from Sudan. Chemicals used for post tanning were of commercial grade; while the chemicals used for the analysis of leather and spent liquors were of analytical grade. The required amount of ground Sunt (*Acacia nilotica*) bark powder was used in re-tanning.

Retanning formulations

The goat wet-blue skins were cut along the backbone into two parts. Left sides were taken for experimental retanning trails using sunt bark powder. Right halves were taken for the retanning using wattle as a matched pair control as a comparison for the experimental leathers. The post tanning processes mentioned in Table I and Table II were followed for both experimental and control leathers respectively.

Measurement of hydrothermal stability of leathers

The shrinkage temperature of both control and experimental leathers were determined using the Theis shrinkage tester (McLaughlin and Thesis 1945).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.

Hand evaluation of leathers

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.

Table 1 Experimental Recipe 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	3x 15	pH 5-5.5
Retanning	20	Sunt bark	1 hour	
Fatliquoring	5	Syntheic fatliquor	45 min	
Dyeing	3	Acid brown dye	45 min	Penetration of dye was checked
Fatliquoring	5	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

Table 2 Control Recipe 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	Wattle	1 hour	
Fatliquoring	5	Syntheic fatliquor	45 min	
Dyeing	3	Acid brown dye	45 min	Penetration of dye was checked
Fatliquoring	5	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

Physical testing

Samples for various physical tests from experimental and control crust leathers were obtained as per IULTCS methods (IUP 2, 2000). 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, (IUP 6, 2000) grain crack strength (IUP 9, 1996) and tear strength (IUP 8, 2000) were measured as per standard procedures. Each value reported is an average of four (2 along the backbone, 2 across the back bone) samples.

Analysis of spent 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 (Clesceri et al., 1989).

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 (Official Methods, 1965). Triplicates were carried out for each sample and the average values are reported.

3. Results and Discussion

Shrinkage temperature

Shrinkage is a phenomenon, associated with dimensional changes of hide, skin or leather when subjected to heating. The temperature at which the material shrinks is termed as "shrinkage temperatur" (T_s); an this varies when the hide or skin is tanned. Shrinkage temperature value (T_s °C) of a specimen in water as the heating medium, is taken as measure of hydrothermal stability and the boil test (viz, test for curling of leather in boiling water) is used even today, to assess the completion of chrome tanning (Kedlaya 1987). The shrinkage temperature of wet blue crust leathers retanned using sunt bark powder and wattle is given in Table III. The wet blue leathers resulted in shrinkage temperature of 109 °C; however the retanning with wattle and sunt bark powder resulted in increase of shrinkage temperature to 116 °C and 113 °C respectively. It is obvious that the treatment of sunt bark improves the shrinkage temperature significantly similar to the case of wattle; hence retanning with sunt bark appears to be a promising option in terms of its reactivity with the leather matrix.

Table 3 Shrinkage temperature of crust leathers retanned with Sunt bark and wattle

Sample	Shrinkage temperature, Ts (°C)
Wattle (Control)	116±2
Sunt bark Experimental)	113±2

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

Tactile properties of sunt bark *retanned leathers*

Control and experimental crust leathers were evaluated for various organoleptic properties by hand evaluation. The organoleptic properties of leathers retanned using sunt bark and control wattle is given in Fig 5. From the figure it is observed that retanning with sunt bark resulted in leathers with good grain tightness and roundness compared to wattle retanned leathers. The fullness of of leathers with wattle retanning is found to be better than that of sunt bark. However, the softness of leathers with sunt bark retanning is found to be better than that of wattle. The grain smoothness of sunt bark retanned leathers has been found to be similar to that of wattle retanning. On the whole the leathers retanned with sunt bark had been found to be better than wattle retannng. The results show that the sunt bark powder has a retanning filling ability and can markedly improve the organoleptic properties of the leather.

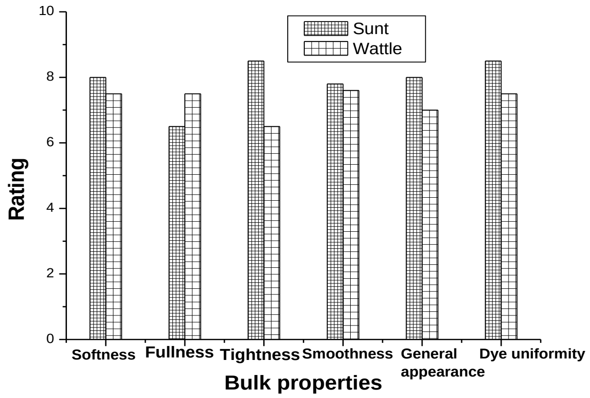

Figure 5: Graphical representation of organoleptic properties of the experimental and control leather

Dyeing Characteristics of Sunt Bark Retanned Leathers

The dyeing characteristics of sunt bark and wattle retanned leathers have been evaluated by experienced tanners and the results are given in Table IV. The uniformity of dye of the sunt bark retanned leathers has been found to be better than the wattle retanned leathers. The shade intensity of the sunt bark 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 sunt bark and wattle retanned leathers.

Table 4 Visual evaluation of the dyeing characteristics of crust leathers retanned with sunt bark and wattle

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

Physical strength characteristics of sunt bark *retanned leathers*

The physical strength measurements of matched pair sunt bark retanned experimental and wattle retanned control leathers are given in Table V. 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 sunt bark retanned leathers have been found to meet the norms for chrome retanned leathers. (BIS, 1964).

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

Property	Sunt bark	Wattle	BIS norms*
Tensile strength (Kg/cm2)	254.55± 17.8	252±19.8	250
Elongation at break (%)	61. 30± 10.42	64. 40 ± 3.70	60-70
Tear strength (Kg/cm thickness)	38.98± 8.546	42.43± 4.56	30
Load at grain crack (kg)	25±5	27±7	20
Distention at grain crack (mm)	10.33± 0.66	11.50± 0.50	Min 7

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

Spent liquor Analysis

The COD, BOD5 and TS of the spent liquor for both experimental and control trials were determined and are given in Table VI. From the table it is observed that the COD and BOD of the spent liquor processed using sunt retanning is lesser than the spent liquor from wattle retanning. However the solid content of sunt retan liquor has been observed to be higher than the wattle retan liquor. Even though the solid content of the sunt retan liquor is higher, the degradability of the same is easier than the wattle retan liquor.

Chemical Analysis of the crust leather

The chemical measurements of matched pair experimental crust leather (*sunt bark*) and control (wattle) are given in Table VII. 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 (*sunt bark*).

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

Parameter	Wattle (Control)	Sunt (Experimental)
COD (mg/l)	89980±3000	71780±1100
BOD_5 (mg/l)	30450±850	27500±750
Total solid (mg/l))	23550±800	32480±850

Table 7 Chemical Analysis of crust leather of experimental and control

Parameter	Sunt bark (experimental)	Wattle (control)
Moisture %	14.20	15.00
Total ash content %	4	4.3
Fats and oils %	5.7	6.2
Water soluble matter %	5.2	6.0
Insoluble ash %	1.70	1.55

Conclusion

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. Most organoleptic properties of the experimental leathers produced from sunt bark powder 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 sunt bark also facilitates in intense dyeing. Hence using sunt bark appears to be a good substitute retanning agent for the retanning processes. Further study is required to find effective application of sunt bark powder in leather making..

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