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RESEARCH ARTICLE

Alternative Combination Tanning System Based on Haraz and Aluminium for High Stability Leather

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Abstract: **The combination of vegetable tannins with metal salts has been used for thousands of years. In the present study, a combination tanning system based on Haraz-Aluminum tannage for the production of upper leathers as a cleaner alternative is presented. Extract from the barks of widely distributed *Faidherbia albida* (Haraz) from Sudan has been evaluated for its tanning characteristics in a combination tanning system based on Haraz and Aluminum sulphate. Both tanning systems Haraz followed by Aluminum (Haraz -Al) and Aluminum followed by Haraz (Al-Haraz) have been attempted. Haraz-Al leathers tanned using 20% Haraz; followed by 2% Al_2O_3 resulted in shrinkage temperature of 100°C. However, Al-Haraz leathers tanned using 2% Al_2O_3; followed by 20% Haraz resulted in shrinkage temperature of 98°C. Haraz-Al combination system resulted in leathers with good organoleptic and strength properties. The work presented in this study established the use of Haraz aluminium combination tanning system as an effective alternative cleaner tanning process.**

Index Terms- **Aluminium sulphate, Haraz, combination tanning, leather, *Faidherbia albida.***

1. INTRODUCTION

During the past few decades combination tannages have been developed to avoid the use of chrome, such as tannages of vegetable tannins with aldehyde compounds or with metal tanning agents [1, 2, 3]. Among these tannages, the combination of vegetable tannins and aluminium is a promising option that produces leathers with high hydrothermal stability comparable to that of chrome-tanned leather [4]. Up to now, leather tanning is dominated by the use of chromium (III) salts, because it gives leather with unmatchable hydrothermal stability and excellent organoleptic properties [5]. 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 [6]. The chromium (III) existing in leather might be transformed into chromium (VI) in some extreme conditions [7]. 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 [8]. In fact, some countries have restricted the use of chrome-tanned leather for certain purposes [9].

Most of the definitions of vegetable tannins quote that they are water soluble (Fig. 1) plant polyphenolic molecules having molecular weight between 500-3000 D. Vegetable tanning has been considered as a suitable ecofriendly option to replace chromium. However, vegetable tanning has some shortcomings such as the fullness of veg leathers which prevents its use for some end products. Vegetable tannins are also difficult to biodegrade [10]. 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 in the western part of the country, particularly in the Jebel Marra area. The tree does not grow on

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iron soils or waterlogged sites. *Acacia nilotica* and *A.seyal* can

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 coloured flowers, and thorns [12, 13]. It is common and widely distributed across Senegal to Northern Nigeria, and extending from Sub-Saharan Africa to Egypt and in East Africa Southward to the Transvaal [14]. The phytochemical analysis of the crude methanolic stem bark extract of *Faidherbia albida* revealed the presence of tannins, saponins and alkaloids. The in vitro antimicrobial activity of the crude methanolic extract of the stem bark showed highest activity on *Salmonella typhi* with zone of inhibition of 12.0±0.17mm compared to *E. coli*

be found mixed with *F. albida* in Sudan [11]. and *Shigella sp*. [15]. The aqueous extract of *F. albida* possesses potent anti-pyretic, anti-inflammatory and antidiarrheal effects and this pharmacologically justifies its folkloric use in the management of fever, rheumatic inflammatory conditions and diarrhoea. In Northern Nigeria, West Africa, the cattle-rearing nomads take a decoction of the stem bark orally for the management of sleeping sickness (trypanosomiasis) [16]. Anti-malarial activity of ethanolic stem bark extract of F.albida against early infection, curative and prophylactic effect in mice at safe doses was also reported [17]. Recently, haraz has been established as an alternative retanning material for wattle [18]. The chemistry of the constituents of *Faidherbia albida* has been of interest.

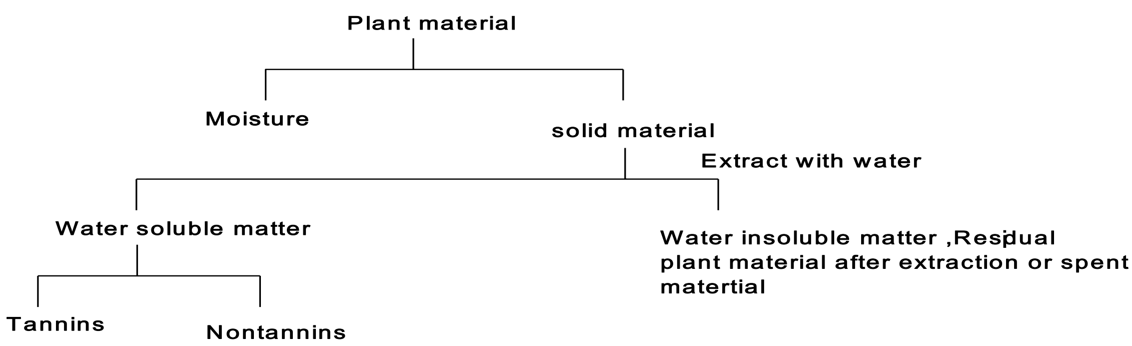

Figure 1: Tannin bearing plant materials

The characteristic features of aluminium salts are a) available in plenty, b) cheaper, and c) have less impact on the environment. Aluminium salts are known to be potential tanning agents for producing leather. However, each of other tanning agents has associated disadvantages [19, 20]. Since haraz extract contain a mixture of several compounds with varied molecular weight including tannin (polyphenols), an attempt has been made in this study, to evaluate the combination tanning system with aluminum sulfate.

II. MATERIALS AND METHODS

Materials

Conventional processed pickled goat skins have been taken for tanning trials. *Haraz* (*Faidherbia albida*) barks from Sudan have been used for the study. Chemicals used for post tanning processes have been of commercial grade.

Aqueous extraction of tannins from Haraz barks

Ground haraz (*Faidherbia albida*) barks of known quantity have been soaked in water (1:10 w/v) at a temperature of 80±2°C in water bath for one hour, filtered through a piece of cotton cloth and concentrated and used in combination tanning.

Preparation of basic Aluminum sulphate solution

A known amount of Aluminum sulphate (2% Al_2O_3 from the weight of pickled goat skins) 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

Haraz -Al sulphate combination tannage

Pickled goat skins have been used for combination tanning trials; Al- Haraz tanning and Haraz -Al tanning process are given in Table 1 and 2 respectively. The amount of Aluminum

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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 Haraz 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

Hydrothermal stability is the measurement of the resistance of a material to wet heat. In the case of collagenic materials, pelt or leather, it is the effect of heat on water saturate material. The shrinkage temperature of control and experimental leathers has been determined using Theis shrinkage tester [21]. 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.

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.

Physical testing

Samples for various physical tests from experimental and control crust leathers have been obtained as per IULTCS methods [22].Specimens have been conditioned at $20\pm2\,^{o}C$ and 65 ± 2 % R.H over a period of 48 hrs. Physical properties such as tensile strength, percentage elongation at break [23], grain crack strength [24] and tear strength [25] 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).

Chemical Analysis

The chemical analysis of the leathers viz. for total ash content, % moisture, % oils and fats, % total ash , % water soluble and % insoluble ash were carried out for control and experimental leathers as per standard procedures [26]. Triplicates were carried out for each sample and the average values are reported.

Table 1. Formulation of the Haraz –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	Basyntan P (phenolic syntan)	30	
	10	Haraz extract	120	
	10	Haraz extract	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.

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Table 2. Formulation of Aluminum- Haraz 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
Haraz tanning	2	Basyntan P (phenolic syntan)	30	
	10	Haraz extract	90	
	10	Haraz extract	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. Formulation of control Haraz 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	Basyntan P (phenolic syntan)	30	
	10	Haraz extract	120	
	10	Haraz extract	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

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Table 4. Formulation 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
Pre-retannage	100	Water		
	2	Acrylic syntan	40	
Pre-fatliquor	2	Synthetic fatliquor	40	
	2	Basyntan DI	30	
Dyeing	3	Acid dye brown	30	
Fatliquoring	3	Synthetic fatliquor		
	4	Lipoderm liquor SAF (Synthetic fatliquor)	40	
Retanning	3	Basyntan DI		
	4	Phenolic syntan	40	
Fixing	1	Formic acid	3× 10 + 30	pH 3.5

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

Table 5. Shrinkage temperature and % exhaustion of control and experimental tanning processes

Experiment	Shrinkage temperature (°C)
AL-Haraz (2% Al_2 O_3)	98±1
Haraz -Al (2% Al_2 O_3)	100±1
Haraz (Control)	85±1

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

III. RESULTS AND DISCUSSION

Combination tanning trials using Haraz and Aluminum sulphate were carried out with Al_2O_3 at a concentration of 2% and 20% offer of haraz. The shrinkage temperature data of leathers tanned with Haraz –Al and Al- Haraz combination along with Haraz 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 (Haraz tanned). The shrinkage temperature of leathers obtained from Haraz-Al combination tanning is higher than Al- Haraz and this experiment resulted in leathers with shrinkage temperature of 100°C, which is much better than control Haraz leather of Ts 85°C. From Table 5, it can be observed that Haraz -Al combination tanning system resulted in enhancement of shrinkage temperature similar to that of wattle-Aluminum combination tanning system.

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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. 2. Higher numbers indicate better property. From the figure, it is observed that Haraz-Al combination tanned experimental crust leathers exhibited good fullness compared to Haraz control leathers. The organoleptic properties of the Haraz -Al crust leathers are better compared to Al-Haraz crust leathers. This is primarily due to improved penetration and fixation of Haraz 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 overall appearance of optimized experimental leathers is better than that of control and other experimental leathers.

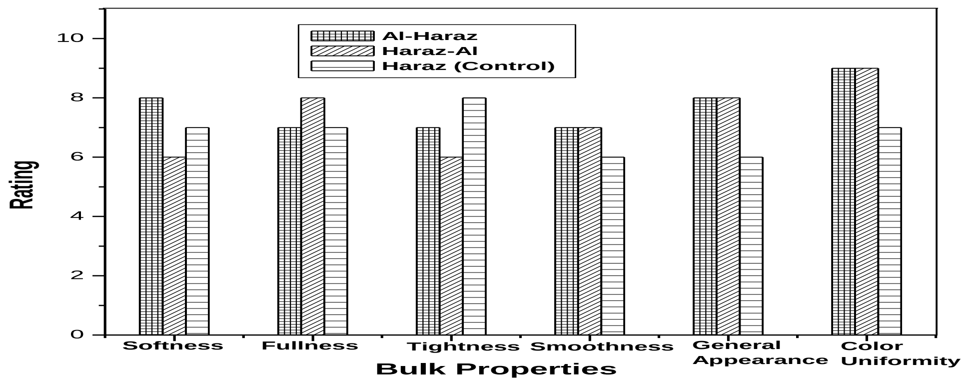

Figure 2: Graphical representation of organoleptic properties of the Experimental and control leather

Physical testing of experimental and control crust leathers

It is essential to study the influence of the tanning system on the strength properties 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 6.

It is observed that the strength characteristics like tensile strength, elongation, tear strength of Haraz -Al tanned crust leathers is found to be higher compared to that of the control and Al-Haraz tanned crust leathers, whereas load at grain crack and distension at grain crack of both control and Al-Haraz tanned leathers are found to be marginally lower.

Table 6. Physical strength characteristics of experimental and control crust leathers

Parameter	Al-Haraz	Haraz-Al	Control (Haraz)
Tensile strength (Kg/cm^2)	251±3	254±4	220±3
Elongation at break (%)	48 ±0.66	57±0.64	42±0.78
Tear strength (Kg/cm)	43±0.72	47±0.75	41±0.70
Load at grain crack (Kg)	25±0.82	23±0.74	27±0.87
Distention at grain crack (mm)	11±0.66	12±0.66	11±0.86

Chemical analysis of the crust leather

The chemical analysis of crust leathers from control and experimental tanning trials 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 leathers is more than the experimental leathers.

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

Parameter	Al-Haraz	Haraz-Al	Control (Haraz)
Moisture %	13	12.20	11.5
Total ash content %	3.5	3.20	3.6
Fats and oils %	5.40	5.60	5.30
Water soluble matter %	4.00	3.20	5.15
Insoluble ash %	1.60	1.40	1.31

Haraz - 20%; Al_2O_3- 2%

IV. CONCLUSION

The selection of tanning agents for combination tanning should be carried out judiciously to avoid competitive fixing. In the present study, an attempt has been made to produce upper leathers using a new eco-friendlier combination tanning process based on Haraz and Aluminum. It is seen that combination tanning using Haraz (20%) followed by Aluminum (2% Al_2O_3) resulted in leathers with shrinkage temperature of 100^oC, which is 15^oC more than the control (Haraz tanned) leathers. Aluminum followed by Haraz tanning resulted in leathers with shrinkage temperature 98^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 Haraz 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.

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