Sunt Bark (Acacia nilotica) Powder Combination Tanning for Manufacture of Upper Leather

Abdella M.H, Musa A.E, Ali S.B

Abstract— **When certain polyphenols and polycarboxyl group compounds are combined with metallic salts (not including chromium) a combination tanned leather is produced with good resistance to hydrothermal shrinkage and a "chemical effect" near to chrome tanned leather. The combination of vegetable tannins with metal salts has been used for thousands of years. The shrinkage temperature of semi-metal tanned leather is much higher than expected. This is an example of synergy, when the total effect is greater than the sum of the parts. In this study, combination tanning process based on Sunt (garad) bark – Aluminum tannage for the production of upper leathers is presented. The bark powder of Acacia nilotica (Sunt bark) from Sudan has been utilized in the combination tanning system with aluminum. Both tanning methodologies Sunt bark followed by Aluminum (Sunt bark -Al) and Aluminum followed by Sunt bark (Al- Sunt bark) have been attempted. All combinations tanning systems resulted in leathers with shrinkage temperature above 90oC. However, Al- Sunt bark leathers tanned using 2% Al2O3; followed by 20% Sunt bark resulted in shrinkage temperature of 96oC. It is seen that combination tanning using Sunt bark (20%) followed by Aluminum (2% Al2O3) resulted in leathers with shrinkage temperature of 100oC, which is 16oC more than the control (Sunt bark tanned) leathers. The spent tan liquor analysis shows significant reduction in COD and TDS loads compared to a conventional vegetable tannage. Sunt bark -Al combination system resulted in leathers with good organoleptic and strength properties. The work presented in this paper established the use of Sunt bark - aluminum combination tanning system as a suitable alternative for chrome-free tanning system.**

Index Terms— **Sunt bark, Garad bark, Aluminum, Combination tannage**

I. INTRODUCTION

The tanning process is based on the conversion of putrescible skin or hides to a non-putrescible material. Leather making involves operations like soaking (rehydration), liming, deliming, pickling, tanning, posttanning and finishing processes.[1] Vegetable tannins have been used for conversion of animal hides to leather for many thousands of years. Man's relationship with plant polyphenols is ancient, since they are components of plant materials and hence are a traditional feature of our diet. Modern interest usually centres on the anti-oxidant properties, which means they can scavenge carcinogenic and mutagenic oxygen free radicals in the body. However, polyphenols are also associated with other physiological reactions of importance, such as accelerating blood clotting, reducing blood pressure and lowering blood serum lipid concentration [2].

Tannins are extracted from plant materials that contain commercially viable concentrations: this may be done with water or with organic solvents. The extracts typically contain three fractions of materials: non-tans, tans and gums [3]. The family of plant polyphenols is characterised by the presence of phenolic hydroxyls, capable of reacting with collagen, at the basic groups on sidechains and at the partially charged peptide links via hydrogen bonding (Fig. 1) [4].

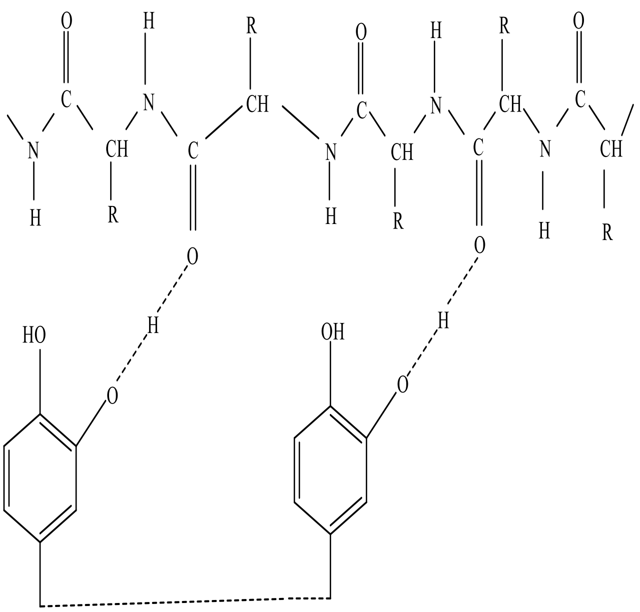

Figure 1. Model of the interaction between plant polyphenol and collagen[4]

Plant polyphenols can be classified into the following three groups, based on their structural characteristics: (i) hydrolysable tannins, with subgroups gallotannins and ellagitannins, (ii) condensed tannins and (iii) complex tannins [5]. The leathers processed through vegetable tanning have advantages such as compatibility with human skin, comfort, and high dimensional stability [6,7]. The tanning methodology adopted also affords easy disposal of spent liquors. But it calls for overcoming the inherent shortcomings associated with the traditional vegetable tanning system, which are inadequate strength, lack of softness, poor fastness properties and highly susceptibility for fungal attack.

Chrome tanning is one of the most popular tanning systems because of the excellent qualities of chrome tanned leather

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such as high hydrothermal stability, good dyeing characteristics and softness [8]. However, chrome tanning is facing great challenges due to environmental impact and increasing market demand for chrome-free leather [9-11].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 [12-14]. Among these tannages, the combination of vegetable tannins and Al is a promising option that produces leathers with high hydrothermal stability comparable to that of chrome-tanned leather [15].

To the rural tanner of tropical and subtropical Africa and Asia, the acacias are one of the most important tannin-bearing trees. Several species, suc h 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) [16].

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 [16]. The elevated concentrations of condensed and hydrolysable tannins obtained from sunt pods point to the possibility of utilizing sunt pod extract in tanning or re-tanning of leather rather than using traditional tanning reagents [17].

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 [18]. The aim of this study to evaluate the combination tanning system of sunt bark with basic aluminum sulphate for making shoe upper leathers, since sunt bark extract contains a mixture of several polyphenolic compounds with varied molecular weight.

II. MATERIAL AND METHODS

Materials

Conventional processed [19] pickled goat skins have been taken for tanning trials. Sunt (garad) bark sourced from Sudan has been used for the study. Chemicals used for post tanning processes have been of commercial grade. Chemicals used for the analysis of spent liquor have been of analytical reagent.

Preparation of Aqueous extraction of Tannins from Sunt Bark

Dry sunt barks obtained from Sudan were grounded into powder. Ground Sunt barks of known quantity have been soaked in water (1:10 w/v) at a temperature of 80±2^{o}C in water bath for one hour, filtered through a piece of cotton cloth and concentrated and used in combination tanning. The total soluble content of the sunt bark extract was determined to be 37±1%.

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

Sunt bark -Al sulphate combination tannage

Pickled goat skins have been used for combination tanning trials; Al-Sunt bark tanning and Sunt bark-Al tanning process 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 Sunt bark 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 shrinkage temperature of control and experimental leathers has been determined using Theis shrinkage tester [20]. 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
Recipe of Sunt bark-aluminum combination tanning system for pickled goat skin.

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	100	Water		
	1	Sodium bicarbonate	3*15	pH 4.5-4.7
Tanning	2	Phenolic syntan	30	
	10	Sunt bark powder	120	
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	2	Al_2O_3 (prepared Aluminum Sulphate solution)	90	
Basification	1	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

Physical testing and hand evaluation of leathers

Samples for various physical tests from experimental and control crust leathers have been obtained as per IULTCS methods [21]. 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 [22], grain crack strength [23], tear strength [24] and flexing endurance [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). Experimental and control crust leathers have also been 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 values indicate better property of leathers.

Table II
Recipe of Aluminum - Sunt bark combination tanning system for pickled goat skin

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	1	Sodium bicarbonate	3 X 15	pH 4.5 -4.7
Tanning	2	Phenolic syntan	30	
	10	Sunt bark powder	90	
	10	Sunt bark powder	90	
Fixing	0.5	Formic acid	3 X 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.

Analysis of spent liquors from tanning trials

The spent tannin liquor from control and experimental tanning processes have been collected, filtered and analyzed for chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), and total dissolve solids (TDS) as per standard procedures [26].

Evaluation of chemical constituents in leathers

The chemical constituents such as total ash content, % moisture, % oils and fats, % water soluble, % hide substance, % insoluble ash and degree of tannage have been carried out for control and experimental leathers according to standard procedures [27].

III. RESULTS AND DISCUSSION

.Combination tanning using sunt bark powder – Aluminum oxide with a Al_2O_3 offer of 2%, keeping the sunt bark offer of sunt bark constant at 20%, and changing the order of addition was carried out. Though, the tanning system using sunt bark and Al_2O_3 are eco friendlier, it is essential to study the properties of the leathers whether it is comparable to that of chrome tanning system. The thermal stability of chrome tanned leathers is well known to be greater than 100°C. The shrinkage temperature data for various combinations are given in Table V. It is seen from the table that just by the use of 2% of Al_2O_3 in combination with sunt bark powder exhibited more than 10°C increase in shrinkage temperature compared to sunt bark powder control leathers. The sunt bark –aluminum oxide combination tanning provides shrinkage temperature of 100°C compared to 84°C for control.

Table III
Recipe of control Sunt bark 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	Sunt bark powder	120	
	10	Sunt bark powder	120	
Fixing	0.25	Formic acid	3 X 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

Organoleptic properties of crust leathers for experimental and control

The organoleptic properties (visual assessment) of upper crust leathers for experimental and control are shown in Fig. 2. From the figure, it is observed that crust leathers processed by experimental combination tanning system exhibited good softness, fullness, smoothness, general appearance and dye uniformity compared to control leathers from sunt bark tannage. The organoleptic properties of the Sunt bark -Al crust leathers are slightly better compared to Al- Sunt bark crust leathers.

Table IV
Recipe of Post-tanning process for control and experimental leathers

Process	%	Product	Duration (min)	Remarks
Washing	200	Water	10	
Neutralization	150	Water		
	1.5	Sodium formate	30	
	1	Sodium bicarbonate	3× 15	pH 5-5.5
Retanning	100	Water		
	2	Acrylic syntan	45	
	9	Phenolic syntan	45	
Fatliquoring	9	Synthetic fatliquor	90	
Dyeing	3	Acid dye brown	30	
Fixing	1	Formic acid	3× 10 + 30	pH 3.5

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

Physical strength characteristics of experimental and control crust leathers

The physical strength measurements of experimental and control leathers are given in Table VI. The physical strength measurements viz., tensile strength, tear strength has been found to be better for experimental leathers. The experimental Sunt bark –Al a tanning system resulted in leathers with good tensile and tear strength characteristics. The values for load at grain crack and flexibility for both experimental and control leathers were comparable. All the physical strength parameters for both control and experimental leathers are found to meet the requirement of standards for upper leathers. It is seen that the softness of experimental leathers are better than that of the sunt bark control leathers. This is in accordance with the observations made by subjective evaluation on softness (Fig. 2).

Spent liquor analysis

The spent tan liquor contains highly organic matter in both control and experimental process liquor and it contributes to high COD, dissolved and suspended solids. Hence, it is vital to assess the environmental impact from control and experimental tanning process. 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 sunt bark tanning (control). The BOD_5 and TDS of the spent liquor processed from sunt bark and aluminum combination tanning trials have significantly reduced compared to the spent liquor of control sunt bark tanning trial.

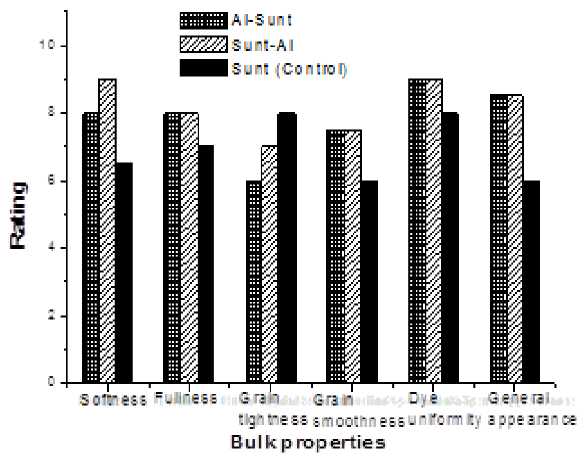

Figure 2. – Graphical representation of organoleptic properties of the Experimental and control leather.

Table V
Shrinkage temperature of control and experimental tanning processes

Experiment	Shrinkage temperature (°C)
Al- Sunt bark (2% Al_2O_3)	96±0.5
Sunt bark -Al (2% Al_2O_3)	100±1
Sunt bark (Control)	84±0.5

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

Chemical Analysis of the crust leather

The chemical analysis values of experimental crust leathers (Al- Sunt bark and Sunt bark -Al) and control (Sunt bark) are given in Table VIII. The chemical analysis data for the experimental leathers is comparable to that of control leathers. However, the water soluble matter for the control leathers is more compared to the experimental leathers.

IV. CONCLUSIONS

Strictly, the term combination just refers to the use of more than one tanning agent. The combination of vegetable tannins with metal salts has been used for thousands of years. The shrinkage temperature of semi-metal tanned leather is much higher than expected. This is an example of synergy, when the total effect is greater than the sum of the parts. In the present study, a new combination tanning system based on Sunt bark and aluminum has been developed as a chrome free tanning. It is seen that combination tanning using Sunt bark (20%) followed by aluminum resulted in leathers with shrinkage temperature of 100°C, which is 16°C more than the control (Sunt bark tanned) leathers. Aluminum followed by Sunt bark tanning resulted in leathers with shrinkage temperature 96°C. The physical and chemical characteristics of experimental leathers are comparable to control leathers. The leather tanned by complex combination tannage has tensile strength and tear strength values meeting the levels of chrome leather. The experimental leathers are softer than the control leathers. The combination tanning using Sunt bark 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 VI
Physical strength Characteristic of experimental and control crust leathers

Parameter	Sunt bark-AL	AL - Sunt bark	(control) Sunt bark
Tensile strength (Kg/cm^2)	246±2	222±2	210±3
Elongation at break (%)	58±1.6	56±0.6	42±1.6
Tear strength (Kg/cm)	60±1.7	51±1.7	48±0.7
Load at grain crack (kg)	25±1.5	22±1.5	24±1.5
Distention at grain crack (mm)	12±0.5	10±1.5	10±07
Flexibility) after 100,000 flexes)	No crack	No crack	No crack

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
Sunt bark (Control)	49400±295	-	25000±900	-	39500±1550	-
Al- Sunt bark	44400±300	10	16500±1100	34	20200±1050	49
Sunt bark -Al	43600±280	13.8	12500±600	50.8	19200±1000	51.4

Table VIII
Chemical Analysis of experimental and control crust leathers

Parameter	Sunt bark **(control)**	**Al-** Sunt bark	Sunt bark **-Al**
Moisture %	14.2	12.3	12
Total ash content %	2.8	2.4	2.2
Fats and oils %	3.3	2.7	3.2
Water soluble matter %	4.8	3.4	3.5
Hide substance %	51	53	52
Insoluble ash %	1.3	1.2	1.6
Degree of tannage %	49.8	51.7	53.3

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