

POTENTIAL OF VEGETABLE TANNING MATERIALS AND BASIC ALUMINUM SULPHATE IN SUDANESE LEATHER INDUSTRY (PART II)

Mahdi Ahmed Haron^{1*}, Palmina Khirstova², Gurashi Abdallah Gasmelseed¹ and Anthony Covington³

Received: Oct 22, 2011; Revised: Feb 17, 2012; Accepted: Feb 20, 2012

Abstract

Ecological pressures on chromium have now forced the leather industry to look for possible alternatives. A vegetable-aluminum combination tannage has been studied, with special attention being given to the intended final product. Aluminum is a mineral tanning agent that is widely used in the leather industry to stabilize collagens. In this study, stabilization of skin collagen by cross-linking vegetable agent and aluminum has been explored. This kind of chrome-free tannage gives us leathers with a shrinkage temperature around 125°C, elongation at break 65.6%, tensile strength of 38 N/mm², and tear strength of 98 N/mm. The chemical properties of the combination tanned leathers offer a product with reduced water solubility and comparable free fats and oil content. A vegetable pre-tanning followed by basic aluminum sulphate retanning was found to produce stronger leather with durable characteristics. In contrast, pre-tanning with aluminum sulphate possibly tightens the collagen fiber network, preventing high molecular weight vegetable tannins from interacting with collagen fibres. Optimal results were obtained when 20% (w/w) vegetable tannin from *Acacia nilotica* pods (garad in the local language) and 5% aluminum sulphate were used.

Keywords: Vegetable, aluminum sulphate, combination tanning, collagen, shrinkage temperature

Introduction

Leather making is a very long process and consists of many different chemical and mechanical process steps. The most important tanning method is chrome tanning which accounts for approximately 85% of the world's heavy leather making. There are many factors governing the tanning effect: the type of the

compound; its basicity, concentration, pH value, and neutral salt content; the temperature of the tanning bath; and the time of interaction, which is long. The previous history of the skin material is also important. Many of these factors are interdependent and difficult to consider separately. The basic chrome tanning chemistry

¹ Bahri University, Industries Dept. P.O. Box 12327, Khartoum, Sudan. E-mail: Mahdikotsh@gmail.com

² People's Hall 11113, P.O.Box 6272, Khartoum, Sudan.

³ University College Northampton, Northampton, UK, Fax- 01604711183

* Corresponding author

is well explained by Gustavson (1956) and Mintysalo *et al.* (1997).

Most attempts to find suitable alternatives for chrome tanning have been undertaken primarily in order to reduce the pollution due to tannery effluents. In certain cases, such efforts were aimed at cost-reduction (Adewoye and Bangaruswamy, 2000).

As regards Sudan, any attempt to reduce the use of chrome has multiple advantages. In the first instance, the Sudanese chrome ores have not yet been confirmed as being commercially exploitable so that the chrome requirements of tanneries are met through imports. The effluents from some of the Sudanese tanneries contain high amounts of chrome exceeding the standards set for discharges into the streams/sewers system (Aloy *et al.*, 1976; Lawal, and Singh, 1981).

The availability of imported chrome tanning agents is also irregular and costly. Mainly for purposes of import substitution, but also for reasons of environmental pollution, studies were conducted towards finding suitable alternative tanning systems to replace or reduce the use of chrome in Sudanese tanneries.

Aluminum has been used in the preservation of skins for centuries. In the form of alum, it was used in the tawing of skins and furs, in an admixture with flour, egg yolk, and salt. Although this helped in the preservation, the skin still lacked resistance to water. The ingredients used, i.e. flour, egg yolk, salt, and alum, can be washed out, as they do not chemically combine with the pelt (the collagen of the skin).

Current studies on the use of aluminum in the leather industry were motivated by demands for a white leather as a substrate for dyeing, the reduction of the environmental impact by replacing chrome, and also the strategic concern over chrome supplies (Covington and Sykes, 1984).

The research and development work since the latter half of the 20th century has oriented towards developing a tanning agent based on aluminum that is stable in solution and will form cross-links with collagen in such a way that real leather, resistant to water and with adequate hydrothermal stability, is

produced. One such stable aluminum tanning agent is the basic aluminum sulphate wherein the aluminum is complexed with citrate anions (Adewoye and Bangaruswamy, 2000). Using this basic aluminum sulphate, in combination with vegetable tannins, other mineral tanning agents, and syntans, almost all types of leathers which were previously tanned with chrome combination systems could be produced (Adewoye and Bangaruswamy, 2000). Aluminum sulphate is indigenously produced on a commercial scale from certain clay deposits in Sudan. So this study provides systematic research on the potential of the combination tannages involving the locally available *Acacia nilotica* ssp *tomentosa* pods (vegetable tannin) and aluminum sulphate with the objective of producing real leather which is resistant to water and with adequate hydrothermal stability.

Materials and Methods

Preparation of Vegetable Tannin Extracts

The weighed quantity of crushed *Acacia nilotica* pods (5 kg) containing the required amount of tannins was soaked overnight in 300% of water (relative to the vegetable mass) and the whole infusion was used the next day.

Preparation of Basic Aluminum Sulphate

Aluminum sulphate ($\text{Al}(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) was dissolved in an equal volume of water, was masked with sodium citrate (8% on the weight of aluminum sulphate), and then basified carefully with soda ash (17.5% on the weight of aluminum sulphate) as a 10% solution. The resultant liquor was approximately 33% basic with 2% Al_2O_3 {i.e. the basicity of ($\text{Al}(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) should be 33%}. It was used after ageing for 48 h.

Tanning Processes

The process was carried out using laboratory drums (small drums used in the lab for tanning purposes) 150 mm wide and 300 mm diameter (height). The industrial chemicals typical of those used in tanneries were used. Four batches of the combination tannage process

were arranged for these tanning processes:

The first batch (B1) consists of *Acacia nilotica* pre-tannage (Veg) and aluminum sulphate retannage (Al). In this batch 20 pieces of pickled sheep skins of fairly similar size and backbone length and free from physical defects were used (the pickled process is a process by which the skins were first treated with 8% salt and 100% water at 25°C (on pelt weight) for 10 min, and then with 1.2% H₂SO₄ for 2 h in a drum, rotating at 12 rpm) (Adewoye and Bangaruswamy, 2000). The skins were thoroughly washed and the pH was adjusted to 4.2 prior to treatment with 20% (on pickled weight) of *Acacia nilotica* extract. After drumming for 3 h with *Acacia nilotica* extract the bath was drained and the skins were left overnight on a horse which is a stand for holding skins for drying. The skins were then given a retannage with basic aluminum sulphate (5% Al₂O₃); this percentage was based on the pickled weight. Thereafter the skins were drummed for 4 h with successive adjustments of pH to 3.9. These adjustments should be made very slowly and carefully to avoid aluminum precipitation. Finally neutralization to pH 4.5 was carried out in a fresh float in order to attain resistance of the tanned skins to boiling water. Then the leathers were piled and dried. The dried leathers were subjected to physical and chemical tests (Adewoye and Bangaruswamy, 2000). The control (20 native pieces) was not tanned but was then dried and subjected to physical and chemical tests as for the B1 (Adewoye and Bangaruswamy, 2000).

The second batch (B2) consists of aluminum sulphate pre-tannage (Al) and *Acacia nilotica* retannage (Veg) compared with the straight or tanneduntanned skins (the control). In this batch 20 pieces of pickled sheep skins were then processed; the skins were pre-tanned with basic aluminum sulphate (5% Al₂O₃), basified to pH 3.8, piled, neutralized, fatliquored, and then retanned with 20% *Acacia nilotica* pods extract using the vegetable infusion already prepared as previously mentioned. This percentage was based on the pickled weight, and then the leathers were piled, neutralized, and dried. The dried leather was

subjected to physical and mechanical operations as for the first batch.

The third and fourth batches were processed in the same way as the first and second batches with the exception that we used 10% aluminum salts instead of 5%, and then the leathers were piled, neutralized, and dried. The dried leather was subjected to physical and mechanical operations as in the cases of B1 and B2.

Chemical Analysis

Preparation of Sample

Leather was cut into small pieces to pass through a screen with circular perforations of 4 mm. The pieces were thoroughly mixed and brought to a state of homogeneity by keeping them in a closed container for at least overnight. After determining their moisture content, they were stored in a jar for further analysis (Borasky and Nutting, 1949).

Determination of Aluminum Sulphate Content

1 g of an aluminum sulphate tanned leather sample was weighed into a 500 ml conical flask. Five ml of concentrated nitric acid followed by 20 ml of oxidizing mixture (perchloric acid/sulphuric acid, 2:1) were added. The mixture was heated in a fume cupboard with the fan on until it turned orange and the heating was continued for 1 minute more. After cooling, approximately 15 ml of cold distilled water and a few anti-bumping granules were added, and then the solution was heated to boiling for 10 min, to remove any free chlorine. The solution was allowed to cool and diluted to 250 ml with distilled water in a volumetric flask; 100 ml of the solution were pipetted into 2 conical flasks and 10 ml of 10% potassium iodide solution were added to each flask, using a measuring cylinder; then the flasks were stoppered and placed in the dark for 10 min. As a starch indicator, 1 ml was added to each flask and they were titrated with 0.1 mol dm⁻³ sodium thiosulphate solution into a pale violet colour (SLTC, 1996).

Calculations

$$\text{Aluminum oxide (Al}_2\text{O}_3\text{), \%} = \frac{T_1 \times 0.0025 \times 100}{M_0}$$

where,

T_1 \equiv volume of sodium thiosulphate that is used in the titration.

1 ml 0.1 N titrant = 0.00173 g Al or 0.00253 g Al_2O_3

M_0 \equiv mass of oven dried sample of aluminum sulphate leather.

Determination of Hide Substances by Total Kjeldahl Method

After determination of the total matter soluble in water, the leather sample was completely dried, and 0.6 g was taken and placed into a dry 250 ml Kjeldhal flask with 15 to 20 ml of concentrated sulphuric acid, as well as some glass beads. The flask was heated gently in the inclined position. The flask was equipped with a small funnel to prevent the loss of acid during the hide destruction. Five g of potassium sulphate and 5 g of copper sulphate were added to the flask, and heated up to boiling until the solution became clear and the colour stopped changing. This procedure took about 30 min. After cooling, the solution was quantitatively transferred into an ammonia distillation apparatus (SLTC, 1996). Through a dropping funnel, sodium hydroxide solution (0.05 M) was added until the solution's colour became black. During the distillation, the quantity of ammonia was reduced to one-third. The ammonia was distilled into 100 ml of sulphuric acid (0.05 M) in the presence of methyl orange as an indicator. Usually, after obtaining about 150 ml distillate it can be considered that all ammonia has been distilled and this procedure takes about 40 min. The excess acid was back-titrated with 0.05 M NaOH (SLTC, 1996).

Calculations

$$\text{Hide substance, \%} = \frac{A \times 100}{B}$$

where,

A \equiv hide substance weight, g

B \equiv leather sample weight, g

Determination of Fat Content

A portion of the sample (20 g) was placed into a Soxhlet apparatus to extract at least 30 siphons using petroleum ether (boiling point 40-60°C) for 5 h. After extraction, the solvent was concentrated under a vacuum to a thick syrup in a tared round bottom flask and then dried in an oven at 103±3°C (SLTC, 1996).

Calculations

$$\text{Fat content, \%} = \frac{100 - a}{b}$$

where,

a \equiv combined fat weight, g

b \equiv weight of leather sample, g

Determination of Total Matter Soluble in Water

The leather samples were used after determination of the fat content; they were dried from the solvent and placed into the conical flask of a shaking apparatus, water was added to cover the samples and the apparatus was shaken for 4 h, then it was left at room temperature (30-36°) overnight. The extract was then collected in a liter volumetric flask and made up to volume with water. Fifty ml of the extract were pipetted into a tared porcelain dish, evaporated on a water bath, then dried in an oven at 100 ± 2°C to constant weight (SLTC, 1996).

Calculations

$$\text{Total matter soluble in water, \%} = \frac{100 \times 20 \times t_2}{t_1}$$

where,

t_2 \equiv residue after drying of 50 ml water extract, g

t_1 \equiv weight of oven dry leather sample, g

Determination of Ash Content

A portion of the prepared sample (5 g) was placed in a porcelain crucible of determined constant weight. First, the sample was carbonized on a hot plate under a fume cupboard and then placed in a furnace at about 800°C until the constant weight was achieved. If it was difficult to burn off all the carbon, concentrated ammonium nitrate solution was added to the residue and it was heated again. If, even after this step, a complete burning off was not achieved, hot water was added to the residue, the solution was filtered, and the residue, on ashless filter paper, was washed. Then it was placed in the same crucible, and then dried to the constant weight (SLTC, 1996).

Calculations

$$\text{Ash, \%} = \frac{100 - t_2}{t_1}$$

where,

t_1 = sample weight, g

t_2 = ash weight, g

Physical Analysis

Conditioning

The specimens for physical testing were kept in a standard atmosphere of temperature $20 \pm 2^\circ\text{C}$ and relative humidity $65\% \pm 2\%$ during the 48 h immediately preceding their use in a test (Adewoye and Bangaruswamy, 2000).

Measurement of Tensile Strength and Percent Elongation

Tensile Strength

The samples were cut parallel and perpendicular to the backbone using a dumbbell shape. The thickness and width of the specimen were measured in the same position using a standard thickness gauge and vernier calipers, respectively, i.e. one measured at the midpoint and the other two at midway. The width must be measured on the flesh and grain side, and

then the mean thickness (mm) and width (cm) are calculated. The area of cross section of each specimen was calculated by multiplying its width by its thickness (SLTC, 1996). The jaws of the tensile machine (Instron 1026, Instron, UK) were set 50 mm apart, and then the sample was clamped in the jaws, so that the edges of the jaws lay along the midline. The machine was run until the specimen was broken and the highest load reached was taken as the breaking load. The tensile strength load is in Newtons (SLTC, 1996).

Calculation

$$\text{Tensile strength} = \frac{\text{Maximum breaking load}}{\text{Cross sectional area}}$$

Percent Elongation at Break

The initial free length between the clamps before and after the final free length at the instant of break was measured. The initial free length was set at 5 cm and the elongation calculated from the graphical readout (SLTC, 1996).

Calculation

$$\text{Elongation, \%} = \frac{\text{Final free length} - \text{Initial free length}}{\text{Initial free length}}$$

Hydrothermal Tension Determination

Hydrothermal tension experiments were carried out in a testing machine (Instron 1112). Using the appropriate load, cells in the range of 0.1-500 kg could be measured. The sensitivity of the load cells was 2% at the maximum range. A liquid cell container was kept on the heater the input supply voltage of which was adjusted to get a required heating rate of $3^\circ\text{C}/\text{min}$. The fibers were immersed in the respective solutions in the liquid cell with 1 end attached to the frame and the other end attached to the load cell. The shrinkage temperature and tension were continuously recorded. As the fiber is held at a constant length during the experiment, the temperature at which the tension begins to increase is recorded as the shrinkage temperature

(T_s). The temperature at which the tension (which increases progressively with shrinkage) reaches the maximum is the temperature at maximum tension (T_i). The corresponding tension is defined as the isometric tension (I_i) (ALCA, 1957; Ramamoorthy *et al.*, 1999).

Differential Scanning Calorimetry Studies for Thermal Properties

The thermal shrinkage temperatures of native, *Acacia nilotica*, and aluminum sulphate tanned rat tail tendon fibers were studied by using a differential scanning calorimeter (DSC 7, PerkinElmer Inc., Mass, USA). The temperature of the instrument was calibrated using indium as the standard. The range of heating of the samples was from 30 to 100°C. The samples were first air dried at the ambient temperature and the weights recorded. One to 2 mg of rat tail tendons were cross-linked in *Acacia nilotica* (20 and 12%) solution at pH 5 and 8 and aluminum sulphate (5 and 10%) solution at pH 2.5 for 24 h, then the *Acacia nilotica* and aluminum sulphate tanned rat tail tendon fibers were swollen in water and 6M urea solution for a period of 24 h.

The samples were sealed in a DSC cell and heated at a constant rate of 5°C/min. The peak temperature, T_p , and the onset temperature, T_s , (in °C), and the enthalpy changes ΔH (in Jg⁻¹) associated with the phase change for the shrinkage process for the native, *Acacia nilotica*, and aluminum sulphate tanned rat tail tendon fibers, before and after urea treatment, were determined (Usha and Ramasami, 2000). After the DSC curve had been obtained, it was fitted to the following equation:

$$D/dT = \beta k_0 e^{-E_a/RT} (1 - \alpha)^n$$

where α is the degree of chemical reaction, n the order of the reaction, k the reaction rate, and β is the proportionality constant. E_a is the activation energy for the phase transition. This equation represents the theoretical shape of the DSC curve that is determined in the PC series, DSC standard program. The resultant values of k_0 , E_a , and n are calculated (Usha and Ramasami, 1999).

Measurement of Tear Strength

This method is intended for use with any types of leather. The specimens were cut as a rectangle 50 mm long and 25 mm wide using a press knife which cuts out the specimen and slot in 1 operation (Template machine) parallel and perpendicular at each position. The Instron 1026 with a uniform speed of separation of the jaws of 100±20 mm per minute was used, and the readings of the load fell into that part of the scale which has been shown by calibration to be correct within 1%. The machine was run until the specimen was torn apart and the highest load reached during tearing was recorded as the tearing load. The tearing load is in Newtons or kilograms (SLTC, 1996).

Assessment of Softness

The leather sample was placed in the tester (ST-300 softness tester, MSA Engineering Systems Ltd., UK) so that it covered the bottom clamp completely. The top arm was lowered by pressing down so that the leather was now clamped in the tester. The load plunger deflects the leather and this deflection is measured and displayed on the dial. Then the top arm release button is pressed and the top arm lifts, allowing the leather to be removed; the actual measurement was obtained by taking the mean value in mm (SLTC, 1996).

Results and Discussions

Tanning is a chemical process by which additional cross-links are introduced into collagen, binding the active groups of tanning agents to the functional groups of protein (Bienkiewicz, 1983). So, the tanning effect mainly depends on the extent of cross-linking between the collagen molecules and the thermodynamic stability of the cross-linking bonds. Animal skins or hides generally have a substantial thickness, thus penetration of tanning agents is also very important for characterizing the tanning process. Only complete penetration and uniform distribution of tanning materials along the hide's cross-section will lead to a satisfactory tanning effect.

All the parameters of the physical and chemical properties were determined and used to describe the tanning effects in this work. As we know, animal hides are not uniform, which means there are big differences in the thickness and type of fibril weaving existing in the different areas of a hide or skin. So, skin pieces from adjacent positions were chosen in each sampling group, one of which served as the control, for every experiment. Results within experiments are comparable (due to samples being adjacent), but results between experiments are not easily comparable, due to inhomogeneities between samplings (Bienkiewicz, 1983).

The introduction of basic aluminum sulphate into the tanning system as a retanning agent produces a definitive improvement in the strength properties of the leather compared with the thatcase where it is used as a pre-tanning agent. The high values for shrinkage temperature, tensile strength, elongation at break, tear strength, and softness in respect of the *Acacia nilotica*-aluminum combination tanned leathers were obtained when using 20% vegetable tannins as pretannage with 5% of aluminum sulphate as retannage compared with 20% and 10% offer respectively (Table 1).

The combination tanned leathers were found to be soft, full, and possessed tight grains compared with native or untanned skin fibers;

these leathers, having better hydrothermal stability, strength properties, and porosity lend themselves to being dyed and fatliquored at higher temperatures to produce different types of leathers intended for varied uses (Table 1) (Thomas and Foster, 1926; Burton *et al.*, 1953; Gustavson, 1956; Selvarangan and Nayudamma, 1965; Metz *et al.*, 2004). On the other hand 20% *Acacia nilotica* pretannage and 5% aluminum retannage also yielded leathers with greater porosity (as evidence by the increased values for water vapor permeability and water intake) (Table 1) .

The hydrothermal stability or shrinkage temperature of the collagen fibers is a measure of the stability of the matrix as a whole, which arises due to the long range ordering of the matrix. The shrinkage temperatures and the temperature at maximum tension of the native skin and tanning using *Acacia nilotica* ssp *tomentosa* pods (vegetable tannins) (20%) and aluminum salts (5%, 10%) were measured using a differential scanning calorimeter (DSC 7, Perkin-Elmer). The shrinkage temperature for the native skin fiber was found to be 65°C (Table 2).

The skin fibers treated with vegetable as a pre-tanning agent exhibited stability against wet heat and the shrinkage temperature for 20% *Acacia nilotica* pre-tanning with different

Table 1. Physical and mechanical properties of native skin and combination of *Acacia nilotica* ssp *tomentosa* pods (veg) (20%) and 5%, 10% Aluminum salts

Characteristics	Native skin (untanned) control	20% Veg pre+5% Al re	5% Al pre20% Veg re	20% Veg pre+10% Al re	10% Al pre 20% Veg re
Elongation at break, %	30.9	70	75.5	20.0	40.0
Softness, mm	1.0	2.9	4.0	2.0	3.0
Water vapour permeability mg/cm ² /h	5.0	7.2	8.0	6.0	3.9
Water uptake during water vapour permeability mg/cm ² /h	100.0	155.0	140.5	145.0	130.5

Pre = pre tanning, *Re* = retanning, *Veg* = vegetable tannin

aluminum retanning percentages was found to be 128 and 115°C, respectively. This due to the increased formation of cross-links and the effects of aluminum, as one of the vegetable–aluminum combination tanning systems, on the stability of the complexes and bond formation, thus increasing the hydrothermal stability of the resultant leathers (Burton *et al.*, 1953; Gustavson, 1956; Selvarangan and Nayudamma, 1965).

On the other hand the skin fibers treated with aluminum as a pre-tanning agent produced a shrinkage temperature of 85 and 80°C, respectively (Table 2). Therefore, it can be concluded from Table 2 that vegetable pre-tanning exhibits an increase in the shrinkage temperature when compared with both the native skin and aluminum pre-tanning. This enhanced hydrothermal stability of vegetable pre-tanning is due to new cross-links formed and consequent changes in the tertiary structure of the skin collagen.

In the case of aluminum retanning, an increase in the shrinkage temperature was observed when compared with the native skin only. This may be due to a net increase in the number of intermolecular cross-links arising from electrostatic and co-ordinate covalent interactions between the aluminum complexes and the skin collagen.

On the other hand the hydrothermal stability of the leather was not improved by

using aluminum as a pre-tanning agent; this was because the synergistic interaction between the polyphenol and the aluminum may arise from the fact that the cross-linking polyphenol on the collagen is itself cross-linked, to form a matrix within the collagen matrix, to stabilize the collagen by the multiplicity of the connected hydrogen bonds in the new macromolecule (Covington and Sykes, 1984; *et al.*, 2006).

The tensile strength and percentage elongation of the native skin and tanning using *Acacia nilotica* ssp *tomentosa* pods (vegetable tannins) (20%) and aluminum salts (5%, 10%) are given in Table 3. On using vegetable pre-tanning and aluminum retanning, the tensile strength increases significantly, until a critical concentration of aluminum as a retanning is reached. Vegetable pre-tanning is capable of diffusing into the molecular pore dimensions. An increase in the tensile strength can be interpreted in terms of the number of covalent cross-links formed during the tanning processes. However, a decrease in the tensile strength at a higher concentration of aluminum retanning (10%) may be due to the increased stiffness (shown by the decreasing elongation) results in a brittle fiber; consequently it breaks more easily at a reduced load. The bound volume measurements of the vegetable pre-tanning and aluminum retanning skin collagen provide an explanation of the increased tensile strength of the vegetable pre-tanning and aluminum

Table 2. Values of shrinkage temperature and temperature at maximum tension on native, and combination tanning using *Acacia nilotica* pods (Veg) (20%) and aluminum salts (Al) (5%, 10%)

Specification	Shrinkage temperature (T _s), °C	Temperature at max. tension (T _t) °C
Native skin	65	68
20% Veg Pretannings+ 5% Al retanning	128±4	>98
20% Veg Pretannings+ 10% Al retanning	115±2	>98
5% Al Pretanning+20% Veg Pretanning	85±3	>94
10% Al Pretanning+ 20% Veg Pretanning	80±2	>94

Note: The values are mean ± S.D. of three values.

retannage skin fiber.

On the other hand the strength properties of the native skin fiber and aluminum pre-tanning and vegetable retanning under the same conditions of temperature vary in the range of 15 ± 4 , 25 ± 3 , and 20 ± 2 MPa, respectively (Table 3). This value of the native skin fiber is nearly the same as those observed for the aluminum pre-tanning and vegetable retanning fiber within experimental errors. In general, aluminum pre-tanning and vegetable retanning does not seem to change the tensile strength of skin fibers significantly in wet condition as well as the vegetable pre-tanning and aluminum retannage; this is due to the fact that the deposition of material with a hardness higher than that of collagen fibers may well reduce the thermomechanical properties (Heidemann, 1993).

The tear strength of vegetable pre-tanning followed by aluminum retanning showed higher values compared with aluminum pre-tanning and vegetable retanning, and with the native skin (Figure 1). This is due to the fact that the fiber bundles are well separated in the case of Al-Veg tanned leather, while Veg-Al tanned leather shows cemented fibers bundles. This would lead to the conclusion that Veg-Al tanned leather would exhibit a high tear strength with low softness, whereas Al-Veg tanned leather would exhibit a low strength with high softness (Figure 1), whilst Al- Veg tanned leather would

show high elongation (Table 3).

The chemical characteristics of the combination tanned leathers are found to be quite normal. The total metal oxide content satisfies the leather requirement compared with the native or untanned skin which has the lowest value (0.5%) (Table 4). The free oils and fats present in the Veg-Al tanned leather {(4.2%) for 20% Veg-5% Al and (7.3%) for 20% Veg-10% Al combinations, respectively} are comparable to those of {Al- Veg (10%) for 10% Al-20% Veg and (15%) for 5% Al-20% Veg combinations, respectively} and the native leather (Table 4). The reduced water solubility (5%) indicates that the aluminum tannages using basic aluminum sulphate ensure better water resistance compared with the native leather (7%) (Table 4) (ALCA, 1957).

The studies thus indicate that vegetable-mineral combination tannages using indigenous *Acacia nilotica* ssp *tomentosa* pods and aluminum sulphate can be easily adopted in the tanneries in Sudan and those in the sub-region. Their use will reduce imports of chrome and will lessen the attendant pollution. Cost-benefit studies may also show considerable benefits for non-Sudanese users of *Acacia nilotica* ssp *tomentosa* pods who may not have access to an indigenous aluminum tanning agent. Depending on the particular quality needed in the final leathers, aluminum can either be used as a pre-tanning or retanning agent.

Table 3. Tensile strength and elongation, % of native skin and combination tanning using *A. nilotica* ssp *tomentosa* pods (Veg) (20%) and aluminum salts (Al) (5%, 10%)

Characterization	Tensile Strength (Mpa)	Elongation, %
Native skin	15 ± 4	30 ± 4
20% Veg Pretanning+ 5% Al retanning	45 ± 4	65 ± 3
20% Veg Pretanning+ 10% Al retanning	35 ± 2	60 ± 5
5% Al Pretanning+ 20% Veg Pretanning	25 ± 3	55 ± 4
10% Al Pretanning+ 20% Veg Pretanning	20 ± 2	40 ± 4

Note: The values are mean \pm S.D. of three values.

Conclusions

The potential of vegetable tanning materials and basic aluminum sulphate in the Sudanese leather industry was investigated. An Instron testing machine, model 1112, has been used for assessing the thermal stability of the collagen. A combination tannage involving a vegetable retanning and aluminum retanning has been found to increase the hydrothermal stability of the produced leather to about 128°C. The sequence of addition of the tanning agents was

shown to be important with the best results from samples tanned first with the vegetable tanning agents then re-tanned with aluminum. In contrast, pre-tanning with aluminum does not improve the hydrothermal stability of the leather because aluminum pre-tanning tightens the collagen fiber network, preventing the high molecular weight vegetable tannins from interacting with the collagen fibres. Another possibility is that the free amino acid side chains of collagens are exhausted on pre-tanning with aluminum, reducing the number of collagen–

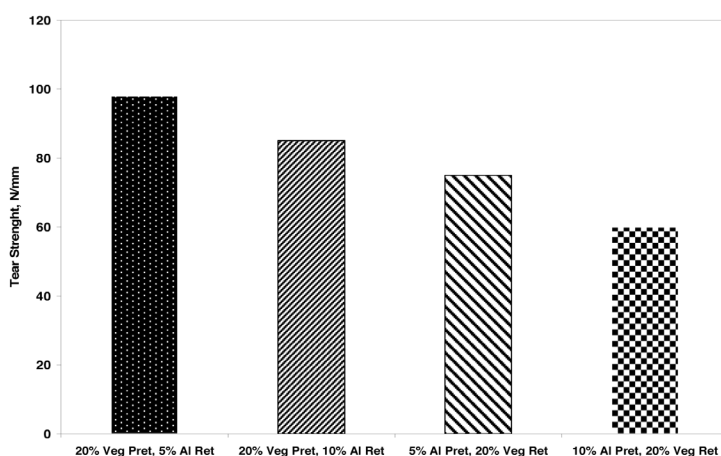


Figure 1. Tear strength of combination tanning using *Acacia nilotica* ssp *tomentosa* pods (vegetable tannins) (20%) and aluminum salts (5%, 10%)

Table 4. Chemical properties of combination tanning using 20% offer *A. nilotica* ssp *tomentosa* pods and 5%, 10 % Aluminum salts (Al)

Characteristics	Native skin (un tanned)	20% Veg pre+5% Al re	5% Al pre+20% Veg re	20% Veg pre+10% Al re	10% Al pre+20% Veg re
Moisture, %	12.0	12.0	10.5	18.0	16.0
Fat content, %	15.5	4.2	15.0	7.3	10.5
Insoluble ash, %	30.0	1.0	3.0	75.0	59.0
Hide substances, %	65.0	78.0	68.0	70.0	67.0
Al ₂ O ₃ -content, %	0.5	1.8	1.5	1.7	1.5
Water soluble, %	7.0	4.0	5.0	3.0	5.0

Pre = pretanning, Re = retanning, Veg = vegetable tannins

aluminum–vegetable tannin cross-links when vegetable tannins are introduced. Optimal results were obtained when 20%(w/w) vegetable tannins and 5% aluminum sulphate were used. In conclusion, we have presented evidence for the possible chemical modifications of collagen brought about by vegetable- aluminum combination tanning. This will further add to our understanding of the tanning of leather that might confirm the mechanism of aluminum tanning as postulated by (DasGupta, 1977).

Acknowledgements

The authors wish like to express their appreciation to the University of Juba, Khartoum, Sudan for the financial support of this research.

References

- Adewoye, R.O. and Bangaruswamy, S. (2000). Acacia nilotica (bagaruwa)-chromium combination tannage—a boon to the leather industry. *J. Soc. Leath. Tech. Ch.*, 73:141-143.
- Aloy, M., Folachier, A., and Vulliermet, B. (1976). *Tannery and Pollution*. 1st ed. Centre Technique Du Cuir, Lyon, France, 100p.
- American Leather Chemists Association (ALCA) (1957). *Methods of Sampling and Analysis*. ALCA., New York, NY, 85p.
- Bienkiewicz, K. (1983). *Physical Chemistry of Leather Making*. Robert E. Krieger Publishing Company, Melbourne, FL, USA, 541p.
- Borasky, R. and Nutting, G.C. (1949). Microscopic method for determining shrinkage temperature of collagen and leather. *J. Am. Leather Chem. As.*, 44:830-841.
- Burton, D., Danby, J.P., and Sykes, R.L. (1953). Hydrothermal stability of combination tannage. *J. Soc. Leath. Tech. Ch.* 37:229-237.
- Choudhury, S.D., DasGupta, S., and Norris, G.E. (2007). Unravelling the mechanism of the interactions of oxazolidine A and E with collagens in ovine skin. *Int. J. Biol. Macromol.* 40(4):351-361.
- Covington, A.D. and Sykes, R.L. (1984). Effect of Aluminum (III) on leather making. *J. Am. Leather Chem. As.*, (3):72-79.
- DasGupta, S. (1977). New postulation for Vegetable Aluminum combination tanning. *J. Soc. Leath. Tech. Ch.*, (3):91-97.
- Gustavson, K.H. (1956). *The Chemistry of Tanning Processes*. 2nd ed. Academic Press, New York, NY., 150p.
- Heidemann, E. (1993). Practical and theoretical aspects of tanning. In: *Fundamentals of Leather manufacture*, Eduard Roether K.G, Darmstadt, Germany, p. 269-294.
- Lawal, F.A. and Singh, K. (1981). Analytical studies of waste water effluents on some tanneries of Kano and Sokoto States for possible environmental pollution. *Bull. Chem. Soc. Nigeria*. 6:68-75.
- Metz, B., Kersten, G.F.A., Hoogerhout, P., Brugghe, H.F., Timmermans, H.A.M., de Jong, A., Meiring, H., ten Hove, J., Henninks, W.E., Crommelin, D.J.A., and Jiskoot, W. (2004). Factors affecting the reaction of Amino groups with Formaldehyde. *J. Biol. Chem.*, 279(8): 6235-6243.
- Mintysalo, E., Marjoniemi, M., and Kilpelfinen, M. (1997). Chrome tannage using high-intensity ultrasonic field. *Sonochem.*, 4:141-144.
- Ramamoorthy, U., Subramanian, V., and Ramasami, T. (1999). Viscoelastic behavior of formaldehyde and basic chromium sulfate crosslinked rat tail tendon (RTT) collagen. *J. Appl. Polym. Sci.*, 71:2245-2252.
- Selvarangan, T. and Nayudamma, A. (1965). Chrome and vegetable tanning combination *Leather Sci.*, 12(2): 249-255.
- Society of Leather Technologists and Chemists, (SLTC). (1996). *Official Methods of Analysis*. 3rd ed. SLTC. Redbourn, UK, 250p.
- Thomas, A.W. and Foster, S.B. (1926). Basic principles for tanning leather with chromium sulphate. *Am. Chem. Soc.*, 6(3): 480-489.
- Usha, R. and Ramasami, T. (1999). Influence of hydrogen bond, hydrophobic and electrovalent salt linkages on the transition temperature, enthalpy and activation energy in rat tail tendon (RTT) collagen fibre, *Thermochim. Acta*, 338:17-25.
- Usha, R. and Ramasami, T. (2000). Effect of crosslinking agents (basic chromium sulfate and formaldehyde) on the thermal and thermo-mechanical stability of rat tail tendon collagen fibre. *Thermochim. Acta*, 356:59-66.

