

VEGETABLE AND ALUMINIUM COMBINATION TANNAGE: ABOON ALTERNATIVE TO CHROMIUM IN THE LEATHER INDUSTRY

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Abstract

Severe restrictions imposed by the pollution control authorities on chromium have forced tanners to look for possible alternatives that are naturally abundant, easily obtainable, low priced, eco-friendly and offer competitive tanned leather performances. In this study, the interactions of vegetable and aluminum, with collagens, have been investigated. This type of combination process helps to improve the shrinkage temperature, percentage of elongation at break, tensile strength, tear strength at 125°C, 65.5%, 38 N/mm², and 98 N/mm, respectively. The combination offers full, soft leathers which have a shrinkage temperature comparable to conventional chrome tanned skins. Among the combination systems evaluated, a vegetable pretannage followed by aluminum retannage was better than the aluminum pre-tanning followed by vegetable retannage. Optimal results were obtained when 10% vegetable tannins and 2% aluminum sulphate were used.

Keywords: Combination tannage, vegetable, aluminum sulphate, shrinkage temperature, collagen

Introduction

Leather tanning is the process of converting raw hides or skins into leather. Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent them from decaying, make them resistant to wetting, and keep them supple and durable. The surface of hides and skins contains the hair and oil glands and is known as the grain side. The flesh side of the hide or skin is much thicker and softer. The three types of hides and skins most often used in leather manufacture

are from cattle, sheep, and pigs. Tanning is essentially the reaction of collagen fibers in the hide with tannins, chromium, alum, or other chemical agents. The most common tanning agents used are trivalent chromium and vegetable tannins extracted from specific tree barks. Alum, syntans (man-made chemicals), formaldehyde, glutaraldehyde, and heavy oils are other tanning agents.

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Although chromium is a “perfect” tanning agent in terms of leather performance, three negative attributes pose serious challenges to continued reliance on tanning with chromium: it is a limited natural resource, its safety record is cautionary and uncontrolled emission can have serious environmental impact. So, reducing dependence on chromium as the “perfect”, primary tanning agent was (and still is) one of the key target areas in current leather research (Skyes, 1988). An effective alternative to chromium must be naturally abundant, easily obtainable, low priced, eco-friendly and offer competitive tanned leather performances. Moreover, it must be easy and safe to use (Tape, 1989). Among the common metal salts with good tanning power, aluminum is abundant in nature, easily obtainable and non-toxic. Aluminum tanned leather has a better performance compared with other metal tanning agents (Heidemann, 1993). So, aluminum tanning is one of the most promising replacements for chromium tanning in today’s leather industry (Gustavson, 1956; Fintysalo *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 streams/sewers system (Aloy *et al.*, 1976; Lawal and Singh, 1983).

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 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 (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, to reduce environmental impact by replacing chrome and also strategic concern over chrome supplies (Covington and Sykes, 1984).

The research and development work since the latter half of this century was 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 basic aluminum sulphate in which the aluminum is complexes 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, were 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 combination tannages involving the locally available *Acacia nilotica* ssp *tomentosa* pods (garad) and aluminum sulphate with the objective of producing real leather, resistant to water and with adequate hydrothermal stability.

Materials and Methods

Preparation of *Acacia nilotica* (garad) Tannin Extracts

The weighed quantity of crushed garad pods (5 kg) containing the required amount of tannins was soaked overnight in 300% of water;

the whole infusion was used the next day.

Preparation of 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 that was masked with sodium citrate (8% of the weight of aluminum sulphate) and then basified carefully with soda ash (17.5% of the weight of aluminum sulphate) as a 10% solution. The resultant liquor was approximately 33% basic with 2% Al_2O_3 . It was used after ageing for 48 h.

Tanning Processes for Production of Leather

The process was carried out using laboratory drums 150 mm wide and 300 mm in diameter. The industrial chemicals typical of those used in tanneries were used.

Two batches of combination tannage process were arranged for these tanning processes:

The first batch (B1) consists of *Acacia nilotica* (garad) pretannage and aluminum sulphate retannage. In this batch 20 pieces of pickled sheep skins of fairly similar size and backbone length and free from physical defects were used (Pickled process is a process by which skins are first treated with 8% salt and 100% water at 25°C (of pelt weight) for 10 min, and then with 1.2% H_2SO_4 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% (of pickled weight) of *Acacia nilotica* (garad) extract. After drumming for three hours with *Acacia nilotica* (garad) extract the bath was drained and the skins were left overnight on a horse. The skins were then given a retannage with basic aluminum sulphate offers (2% Al_2O_3). This percentage was based on 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.

The control (20 pieces) were tanned only with 10% of *Acacia nilotica* (garad) extract (percentage based on pickled weight) and processed further as for Experiment 1.

The 2nd batch (B2) consists of aluminum sulphate pretannage and *Acacia nilotica* (garad) retannage compared to straight *Acacia nilotica* (garad) (control). In this batch 20 pieces of pickled sheep skins were then processed; the skins were pretanned with basic aluminum sulphate (2% Al_2O_3), basified to pH 3.8, piled, neutralized, fatliquored (adding fats) and then retanned with 20% *Acacia nilotica* (garad) extract using the garad infusion already prepared in section 2.1. This percentage was based on pickled weight, and then the leathers were piled, neutralized, and dried. The dried leather was subjected to physical and mechanical operations as in the first batch.

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 its use in the test (SLTC, 1996).

Shrinkage Temperature Determination

The shrinkage temperatures of the tanned skins were measured using a micro-shrinkage meter as described below using the standard method (Borasky and Nutting, 1949). A small strip of fibre was cut and placed on a water-grooved microscope slide. The slide in turn was placed on a heating stage along with a microscope mounted above the heating stage. The rate of heating was maintained at $2^\circ\text{C}/\text{min}$. The temperature at which the fibre shrinks to one-third of its length was taken as the shrinkage temperature.

Measurement of Tensile Strength and Percentage 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, respec-

tively i.e. measured one at the mid point and the other two 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) were set 50 mm apart, and then the sample was clamped in the jaws, so that the edges of the jaws lay along the mid line. The machine was run until the specimen was broken and the highest load reached was taken as the breaking load. Tensile strength load is in Newtons or kilograms (SLTC, 1996).

Calculation

Tensile strength =

$$\frac{\text{Maximum breaking load}}{\text{Cross sectional area}} \quad \text{Units Nm}^{-2} \text{ or kg cm}^{-2}$$

Percentage Elongation at Break

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

Calculation

Elongation, % =

$$\frac{\text{Final free length} - \text{Initial free length}}{\text{Initial free length}} \times 100$$

Assessment of Softness

The leather sample was placed in the tester (ST-300 softness tester) so that it covered the bottom clamp completely. The top arm was lowered by pressing down; the leather was now clamped in the tester. The load plunger deflects the leather and this deflection is measured and displayed on the dial. After the reading was obtained, the top arm released 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).

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 by use of

a press knife which cuts out the specimen and slot in one operation (Template machine) parallel and perpendicular at each position. Instron 1026 has a uniform speed of separation of the jaws of 100 ± 20 mm per minute used, and the readings of load fall in that part of the scale which has been shown by calibration to be correct to 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. Tearing load is in Newtons or kilograms (SLTC, 1996).

Chemical Analysis

Preparation of Sample

The 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 one night. After determining their moisture content, they were stored in a jar for further analysis (ALCA, 1957).

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 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, complete burning off was not achieved, hot water was added to the residue, and 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 a constant weight (SLTC, 1996).

Calculations

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

Where,

$t_1 \equiv$ sample weight

$t_2 \equiv$ ash weight

Determination of Fat Content

A portion of the sample (20 g) was placed

into a Soxhlet apparatus to be extracted by petroleum ether (boiling point 40 - 60°C) for 5 h, at least 30 siphons (recycles). After extraction, the solvent was concentrated in a vacuum to thick syrup in a tarred round bottom flask and then dried in an oven at $103 \pm 3^\circ\text{C}$ (SLTC, 1996).

Calculations

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

Where,

a $\equiv$ combined fat weight, g

b $\equiv$ weight of leather sample, g

Determination of Aluminum Sulphate Content

1 g of full aluminum sulphate was weighed into a 500 ml conical flask. 5 ml of concentrated nitric acid was added followed by 20 ml of oxidizing mixture (perchloric acid/sulphuric acid, 2:1). The mixture was heated in a fume cupboard with the fan on until it turned orange and the heating was continued for 1 min 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 point 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 two 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. Starch indicator, 1 ml was added to each flask and they were titrated with 0.1 mol dm^{-3} sodium thiosulphate solution to a pale violet colour (SLTC, 1996).

Calculations

$$\text{Aluminum oxide (Al}_2\text{O}_3\text{), \%} = \frac{T_1 \times 0.00253}{M_0} \times 100$$

Where,

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

1 ml 0.1 N titrant

= 0.00173g Al or 0.00253 g Al_2O_3

M_0 $\equiv$ mass of oven dry sample of Aluminum

Sulphate leather.

Determination of Total Matter Soluble in Water

The leather samples were used after determination of the fat content, dried from the solvent and placed into the conical flask of a shaking apparatus, then water was added to cover the sample and it was shaken for 4h, then it was left at room temperature ($30 - 36^\circ\text{C}$) overnight. The extract was then collected in a liter volumetric flask and made up to volume with water. 50 ml of the extract was pipetted into a tarred porcelain dish, evaporated on a water bath, then dried in an oven at $100 \pm 2^\circ\text{C}$ to constant weight (SLTC, 1996).

Calculations

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

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 Hide Substances by Total Kjeldahl Method

After determination of the total amount of matter soluble in water, the leather sample was completely dried, and 0.6 g were 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 loss of acid during hide destruction. 5 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 ammonia distillatory. Through a dropping funnel, sodium hydroxide solution (0.05 M) was added until the solution 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 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

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

Where,

A $\equiv$ hide substance weight, g

B $\equiv$ leather sample weight, g

Results and Discussion

Tanning is a chemical process by which additional crosslinks are introduced into collagen, binding active groups of tanning agents to functional groups of protein (Bienkiewicz, 1983). So, the tanning effect mainly depends on the extent of cross-linking between 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 cross-section will lead to a satisfactory tanning effect.

Effects of Vegetable Tanning on Kinetics of Aluminum Uptake

Combination tanning was carried out using laboratory drums 150 mm wide and 300 mm diameter, initially 10% vegetable pretanning, subsequently followed by 2% aluminum retanning. The effect of vegetable pretanning on aluminum uptake, during the initial stage of tanning is shown in Figure 1, which shows plots of aluminum uptake versus time with two retanning agent offer levels (2% and 5%). From Figure 1 we can come out with conclusion that using of aluminum as retanning agent is much better than pretanning, this is because aluminum possibly tightens the collagen fiber network, preventing high molecular weight vegetable tannins from interacting with collagen fibers. So, aluminum uptake with 10% Vegetable pretanning is greater than that with vegetable retanning at both 5% and 2% levels. Interestingly, the

differences in aluminum uptake after 3 h is 40 mg Al/g skin for the 2% offer and 20 mg Al/g skin for the 5% offer retanning. Thus, vegetable tanning materials have a larger effect on the 2% offer (lower percentage) than on the higher 5% level.

Chemical Properties of the Combination Tanned Leather

The chemical characteristics of the combination tanned leathers are found to be quite normal. The total metal oxide content satisfies the leather requirement (Table 1). The free oils and fats present in vegetable- aluminum tanned leather are comparable to those of normal tanned leather (Table 1). The reduced water solubles (Table 1) indicates that the aluminum tannages using basic aluminum sulphate ensure better water resistance.

The combination tanned leathers were found to be soft, full and possessed tight grain; 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).

On the other hand 10% offer *Acacia nilotica* pretannage and 2% offer aluminum retannage also yielded leathers with greater porosity (as evidenced by the increased values for water vapor permeability and water intake) (Table 1) .

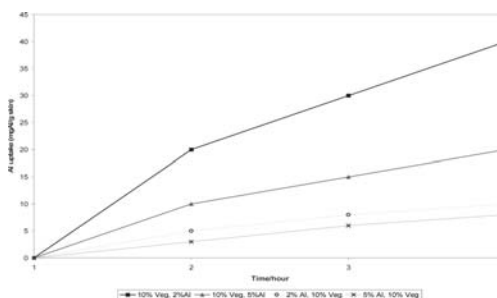


Figure 1. Shrinkage temperature of combination tanning using 10% vegetable tannins of *Acacia nilotica* ssp *tomentosa* pods and aluminum sulphate (2%, 5%)

Physical Properties of the Combination Tanned Leather

The introduction of basic aluminum sulphate into the tanning system as a retannage agent produces a definitive improvement in the strength properties of the leather. The high values for shrinkage temperature, tensile strength, elongation at break, tear strength, and softness in respect of *Acacia nilotica*- aluminum combination tanned leathers, obtained when using 10% vegetable tannins offer as pretannage with 2% offer of aluminum sulphate as retannage agents compared to 10% and 5% offer respectively (Table 2).

Shrinkage Temperature of the Combination Tanned Leather

Shrinkage temperature, defined as the temperature at which a hide or leather sample begins shrinking, is one of the main parameters signaling leather formation. The high shrinkage temperature indicates greater hydrothermal stability due to the increased formation of cross-links (Figure 1). The effects of aluminum, as one component of the vegetable –aluminum combination tanning systems, on the stability of the complexes and bond formation increase the hydrothermal stability of the resultant leathers (Figure 1) (Thomas and Foster, 1926; Burton

Table 1. Chemical properties of combination tanning using 10 % offer *Acacia nilotica* ssp *tomentosa* pods and 2%, 5% aluminum sulphate

Characteristics	10% Veg pre + 2% Al re	2% Al pre + 10% Veg re	10% Veg pre + 5% Al re	5% Al pre + 10% Veg re	Veg tanning (control)
Moisture, %	19.6	20.9	17.8	15.6	16.0
Fat content, %	60.5	55.5	40.5	32.8	50.5
Insoluble ash, %	0.9	2.0	75.0	60.6	60.8
Hide substances, %	125.0	100.0	98.0	85.3	75.0
Al ₂ O ₃ -content, %	1.6	1.3	1.6	1.4	1.2
Water soluble,%	3.0	5.0	3.0	5.0	6.2

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

Table 2. Physical properties of leather using combination of *Acacia nilotica* ssp *tomentosa* pods (veg) (10%) and 2%, 5% aluminum sulphate

Characteristics	10% Veg pre + 2% Al re	2% Al pre + 10% Veg re	10% Veg Pre + 5% Al re	5% Al pre + 10% Veg re	Veg Tanning (control)
Elongation at break, %	60.5	65.5	17.0	32.0	50.5
Softness, mm	2.6	3.8	1.6	3.4	1.2
Water vapour permeability mg/cm ² /hr	6.8	7.9	6.8	7.9	6.2
Water uptake during water vapour permeability mg/cm ² /hr	150.8	130.6	140.8	125.6	120.9

Pre= pre tanning, Re= retanning, Veg= vegetable tannin, Al= aluminum

et al., 1953; Gustavson, 1956; Selvarangan and Nayudamma, 1965; Metz *et al.*, 2004).

The results of shrinkage temperature of combination tanning using *Acacia nilotica* ssp *tomentosa* pods and aluminum sulphate are shown in Figure 1. The shrinkage temperature for 10% *Acacia nilotica* pretanning with different aluminum retanning was found to be 125°C and 110°C, respectively. This is due to the increased formation of cross-links and the effects of aluminum, as one component 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, using aluminum as a pretanning agent did not add any more to the hydrothermal stability of the leather and this is because the synergistic interaction between the polyphenol and the aluminum (III) may arise from one of the following options:

Collagen- aluminum -vegetable- aluminum -collagen
Collagen-vegetable- aluminum -vegetable -collagen
Collagen-vegetable- aluminum -collagen

It is known that applying the aluminum salts before the vegetable tannins produces only moderate shrinkage temperature, with characteristics of aluminum alone (Figure 2). Therefore, the first and third options are unlikely. The most probable mechanism is for the aluminum (III) to crosslink the vegetable tannins. In effect, the crosslinking polyphenol on collagen is itself

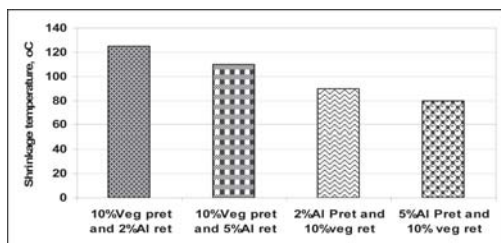


Figure 2. Effect of 10% vegetable tanning on 2% and 5% aluminum uptake as pretanning and retanning agents

crosslinked, to form a matrix within the collagen matrix, to stabilize the collagen by a multiplicity of connected hydrogen bonds in the new macromolecule (Choudhury, *et al.*, 2006).

Strength Properties of the Combination Tanned Leather

Tensile strength and tear strength of vegetable pretanning followed by aluminium retanning showed higher values compared to aluminium pretanning and vegetable retanning (Figures 3 and 4). And this is due to the fact that the fibre bundles are well separated in the case of aluminum -vegetable tanned leather; while vegetable- aluminum tanned leather shows cemented fibres bundles. This would lead to the conclusion that vegetable- aluminum tanned leather would exhibit high tensile strength and tear with low softness where as aluminum

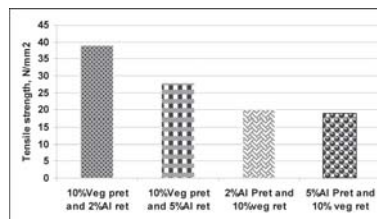


Figure 3. Tensile strength of combination tanning using 10% vegetable tannins of *Acacia nilotica* ssp *tomentosa* pods and aluminum sulphate (2%, 5%)

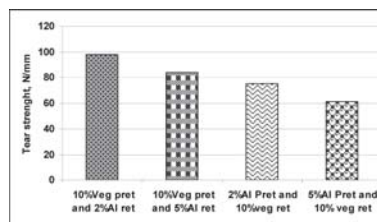


Figure 4. Tear strength of combination tanning using 10% vegetable tannins of *Acacia nilotica* ssp *tomentosa* pods and aluminum sulphate (2%, 5%)

-vegetable tanned leather would exhibit low strength with high softness (Figures 3 and 4). Whilst aluminum - Vegetable tanned leather would show high elongation (Table 1).

The studies thus indicate that vegetable-mineral combination tannages using indigenous *Acacia nilotica* ssp *tomentose* 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 *tomentose* pods who may not have access to indigenous aluminum tanning agent. Depending on the particular quality needed in the final leathers, aluminum can either be used as a pretanning or retanning agent.

Conclusions

In this study, we have shown that a combination tannage involving a vegetable tan (garad) and aluminum sulphate uniquely cross-links collagens, producing leather with high shrinkage temperature around 125°C. The sequence of the addition of the tanning agents was shown to be important with best results from samples tanned first with vegetable tanning agents then re-tanned with aluminum. Previous studies indicate that vegetable tannins are able to penetrate the collagen inter-fibrillar space making the collagen peptide groups more accessible to aluminum tannins. In contrast, pretanning with aluminum possibly tightens the collagen fibre network, preventing high molecular weight vegetable tannins from interacting with collagen fibres. The other possibility is that the free amino acid side chains of collagens are exhausted on pre-tanning with aluminum, reducing the number of collagen -aluminum -vegetable tannin cross-links when vegetable tannins are introduced. Optimal results were obtained when 10% w/w vegetable tannins (garad) and 2% aluminum was used. In conclusion, we have presented evidence for 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, 1997.

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