

## Innovation of New Cleaner Technology: Tannage by Local Tanning Agent *Acacia Nilotica* (Garad) and Aluminum Retannage

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**ABSTRACT** - The present work was carried out to reuse chromium tannage and establish new cleaner technology by using vegetable tanning (garad) with aluminum alternatives to chromium tannage. Twelve pickled cattle hides were treated in pilot drum with speed of 8 rpm in four trails. Used garad (*Acacia nilotica*) as tannage offers vegetable agent (30%) and Aluminum as retannage in different percentage (1, 2, 3, 4 %), followed by 10% garad. Chemical analysis of leather viz. percentage of moisture, ash, and fat were carried out for the experimental leathers. Physical testing including thickness, tensile strength, percentage elongation at break, and shrinkage temperature. The chemical properties of leathers in all trials are found to be quite normal. The shrinkage temperature of experimental leathers for all trails above 70°C, tensile strength that above 215 Kg/cm<sup>2</sup>.

**Keywords:** *Chrome Free Leather, Semi Mineral, Shrinkage Temperature, Elongation, Tensile Strength*

**المستخلص** - تهدف هذه الدراسة لتأسيس تكنولوجيا نظيفة باستخدام القرض والألمونيوم كمادة بديلة للكروم، 12 نصف قطعة جلد بقري محنط عولجت في برميل سرعته 8 دورة في الدقيقة قسمت الي اربع تجارب استخدم 30% من القرض في الدباغة وفي اعادة الدباغة نسب مختلفة من الالمونيوم (1، 2، 3، 4%) الجلود المنتجة اجريت لها الاختبارات الكيميائية وهي نسبة الرطوبة، الرماد والدهن والاختبارات الفيزيائية وهي السمك، قوة الشد، الاستطالة كل الجلود اعطت نتائج كيميائية طبيعية واعطت درجة انكماش اعلي من 70 درجة مئوية وقوة شد اعلي من 215 كلجم لكل سنتمتر مربع.

### INTRODUCTION

Leather is a direct industrial product of a natural fabric, skin. The architectural marvel of skin is yet unmatched by man-made synthetics. The comfort and personal hygiene of leather products have remained unique. Leather processing technology has evolved naturally from a traditional practice to an industrial activity. The leather industry contributes substantially to pollution of the environment. Environmental challenges from leathers processing arise from both of nature and the quantum of wastes discharged [14], [15], [5]. To rural tanner of tropical and sub tropical Africa and Asia, the acacia are one of the most important tannin-bearing

treses. Several species such as *Acacia arabic*, *A. nilotica*, and *A. adamsomia*, have supplied pods and barks since immemorial time, the acacia pods and bark are known variously in the countries where they grow as babul (Hindustan, babar (sindj), garad or sunt (Sudan), babra (Africa), neb-neb (west Africa) and gabarua (Nigeria [11]).

In recent years, considerable research has been done to replace chrome tanning with alternative tanning systems. But there are very few methods that are environmentally friendly and cost effective that give leather with performance as good as chrome tanned leather [3]. Development of cleaner technologies for leather manufacture is

imperative for the sustenance of the tanning industry. A combination tanning system based on a henna-aluminum tannage for the production of upper leathers as a cleaner alternative is presented. Henna-Al combination tanning system resulted in leathers with good organoleptic and strength properties established the use of henna and aluminum combination tanning system as an effective alternative cleaner tanning methodology<sup>[12],[13]</sup>.

The reaction site for aluminium (III) are the collagen carboxys, but unlike chromium (III) to which it bears superficial resemblance in a tanning context, aluminium (III) does not form defined basic species nor does it form stable covalent complexes with carboxyl groups; that interaction is predominantly electrovalent, accounting for the ease of hydrolysis<sup>[1]</sup>.

Vegetable based tanning system in combination with aluminum, zinc, acrylics and oxozolidine has been assessed. Vegetable - aluminum based tanning system has been found to be more suitable for the integrated one step upper leather processing as it has resulted in leathers with shrinkage temperature of 94 °C, good physical strength and organoleptic properties<sup>[9]</sup>. Semi metal tanning system is gaining importance in recent times as an alternative for chrome tanning. Many reports are available regarding vegetable-aluminum combination tanning systems, but the mechanism of interaction between the aluminum and the vegetable tanning molecules has not been elucidated in detail<sup>[10]</sup>.

Vegetable-Aluminum (Veg-Al) combination tanning system was found to be suitable for the manufacture of integrated chrome free upper leather processing<sup>[9]</sup>. The objective of the present

work was to replace chromium tannage and establish new cleaner technology by using vegetable tanning (garad) with aluminum alternatives to chromium tannage Objective of this study is compare these properties with currently produced leather in local market.

### Material and Method

The tannage and retannage were carried out during the period of November 2010 - January 2011 at Sudan University of Science and Technology (Leather Industrial Incubator). The chemical analysis of leather and physical testing were carried out at the National Center of Leather Technology. Khartoum- Sudan.

**Process:** The following processes were carried out in this research for leather manufacturing. All percentages were based on the initial pickled weight. The pickled pelts tanned with 30% garad and retanned with different aluminum offers (1%, 2%, 3%, 4%) followed with 10% garad in four trials.

**Degreasing:** .Degreasing: drum pelts for 30 minutes with 5% common salt 3% degreasing agents (SUPRLAN 80) at 35°C Then add: 100% water at 35°C running for 60 minutes, Then add: 5% common salt 3% degreasing agents (SUPRLAN 80) at 35°C Running for 30 minutes Horse up, overnight.

**Depickling** Pelts washing in 150% solution have 6.7°Be, drummed for 20 minutes, repeated washing 150% solution have 6.7°Be, drummed for 20 minutes drained. Then add: 300% water at 35°C 4% salt of 6.7° Be 0.8% of sodium bicarbonate drummed for 60 minutes this raised pH 3.80.4% sodium bicarbonate drummed for 30 minutes this raised pH 4.5 for tannage process.

**Tannage operations:** Then add: 10% of garad powder, drummed for 45 minutes 10% of garad powder, drummed

for 45 minutes 10% of garad powder, drummed for 45 minutes Then fixation: 0.3% formic acid was added and drummed for 15 minutes 0.3% formic acid was added and drummed for 15 minutes 0.3% preservative agent, drummed for 30 minutes then check pH 3.5 Horse up, overnight.

**Retannage:** Drum pelts for 30 minutes with 300 water at 35°C 6.7°Be salt, pH 3.5 Then add: 0.9% sulphuric acid drummed for 90 minutes Then add: the deferent aluminum offers (1%, 2%, 3%, 4%) and drummed for 90 minutes Then add: 0.25% MgO drummed for 40 minutes, then check pH 3.8 Then add: 1% sodium bicarbonate drummed for 30 minutes then cheek pH 4.5 Then add: 10% garad drummed for 45 minutes Then add: 0.3% formic acid drummed for 15 minute s Then add: 0.01% anti mould agent and 1% sodium bicarbonate drummed for 30 minutes rising pH from 5.5 to 6 Drummed overnight.

**Fatliquoring:** Drum pelts for 45 minutes with 100% of hot water (45-50°C) 3% of sulphonate oils (PELLASTOL OX) Then add: 1% of sulphonate oils (PELLASTO OX) drummed for 45 minutes Then add: 0.75% formic acid drummed for 15 minutes Then add: 0.75% formic acid pelts were drained and rewashed Horse up, left overnight, set out and drying.

**Physical testing and hand evaluation of leathers** Samples for various physical tests from experimental crust leathers have been obtained as per (SLTC, 1996). Specimens have been conditioned at 20+<sub>-</sub> 2°C and relative humidity 65% +<sub>-</sub>2% during 48 hours before use in a test. Physical properties such as thickness tensile strength, percentage elongation at break, grain crack strength, bally flexometer and Shrinkage temperature have been measured as per standard procedures

(SLTC, 1996). Experimental crust leathers have been assessed for softness, fullness, grain smoothness, general appearance and dye uniformity by hand.

**Chemical analysis of leathers:** For chemical analysis, leather of all kinds must be ground in a cutter mill. The ground material obtained from the mill called “ground leather” or “leather powder” (SLTC 1996). Total ash content, % Moisture and % fats carried out for experimental leathers according to standard procedures (SLTC, 1996).

**Statistical Analysis** The data physical and chemical were analysis (ANOVA) using the statistical package for science (SPSS).

**Results and Discussion:** Tanning is a chemical process that converts animal skins and hides into leather by introducing additional cross-links to collagen. The efficiency of tanning depends on the binding activity of the tanning agents to the functional groups in collagen. It also depends on the thickness of the animal skins or hides. Complete penetration of tanning agents to the skin or hide lead to uniform distribution of these agents which will lead to satisfactory tanning.

In this study *Acacia nilotica* (garad) was used as tanning agent at constant concentration (30%). Aluminum was used as retannage agent at different concentrations (1, 2, 3 and 4%). All raw hides used are converted into normal leather with good softness, fullness, smoothness, general appearance, dye uniformity. The use of mechanical effect (drum) in tanning operation in the current study resulted in reduction of tanning time (few hours) compared to very long time in traditional vegetable tannage in pits. This is due to the slow penetration of large reactive molecules<sup>[1][4]</sup>.

Some chemical (Table 1) and physical (Table 2) characteristics of the leather

produced in this study were determined so as to describe the effect of tanning. The moisture content (3.89-6.98%), ash content (1.64-3.53%) and fat content (4.10-6.98) of the produced leather fall within the normal values. The moisture content was significantly affected by the concentration of the Al and it tended to increase with the increase of Al concentration.

However, the moisture content of the leather obtained from re-tanning with 1% Al was significantly lower than that obtained from re-tanning with all other Al concentrations. Resulted in this study found different significant in percentage moisture aluminum in different percentage as retannage. Indicate that aluminum as retannage ensure better water resistance.

There are an abundance of hydrophilic groups in the collagen fibers in leathers. Because the affinity between these hydrophilic groups and water molecules varies with changes in temperature and relative humidity, leathers will adsorb or de-adsorb water as these factors change; affecting strength, permeability, and thermal stability.

Retanning is a key operation in leather making with the purpose of retanning is to obtain leathers with some special characteristics<sup>[7]</sup>. The ash content in the current study (1.64-3.53) was significantly affected by the concentration of Al. However, all values obtained are comparable to those reported by Musa and Gasmelseed<sup>[13]</sup>. A very wide range of ash content (0.9-70%) was obtained by Haroun<sup>[6]</sup>.

The fat % in this study (4.10-6.98) was also significantly affected by Al concentration. The thickness of the leather produced to the different Al concentrations used range between 1.66-1.2.26 mm.

Animal hides are not uniform, which means there are big difference in thickness and type of fibril weaving existing in different areas of a hide or skin<sup>[8]</sup>. All other physical characteristics determined in this study (tensile strength, elongation, grain crack, grain break and shrinkage temperature) showed high values. The Al re-tanning improve the strength properties of the leather. The tensile strength it is the force required to rupture a leather specimen of unit cross sectional area. The tensile strength was thus the combined breaking strength of all the fibers which are taking part to fight against the applied load.

The tensile strength of this semi metal gave competitive results, to produce different type of leathers<sup>[4]</sup>. The percentage elongation at break load properties of vegetable tanned garad with different percentage of aluminum as retannage (1, 2, 3, 4 %) were 35.4, 27.3, 30.6 and 38.3 % respectively. The obtained values are quite normal. The obtained values of the grain crack and grain break in this study are normal and indicate good strength of the leather produced.

The flexibility after 100,000 flexes for the experimental leathers compared with the grey scale indicates good flexibility and the semi metal leathers produced could be accepted for shoe upper leather manufacture. The resistance to flexural fatigue plays an important role among the elasticity properties. One of the most important effects of tanning is to the increase the hydrothermal stability<sup>[1]</sup>. This can be measured by observing the point at which a specimen shrinks, when it held in continuously heated water. Results in this study (Table, 3) show high shrinkage temperature (70-80.1 °C).

**Table (1): Effect of Aluminum as retanning on some chemical characteristics of cattle leather**

Parameter Aluminum conc.	Moisture (%)	Ash (%)	Fat (%)
1%	3.89±0.7 <sup>b</sup>	1.64±0.0 <sup>d</sup>	4.27±0.3 <sup>b</sup>
2%	6.72±0.3 <sup>a</sup>	3.53±0.2 <sup>c</sup>	6.98±0.1 <sup>a</sup>
3%	6.98±0.1 <sup>a</sup>	3.00±0.0 <sup>a</sup>	4.10±0.1 <sup>b</sup>
4%	6.43±0.1 <sup>a</sup>	2.70±0.2 <sup>b</sup>	4.27±0.3 <sup>b</sup>
Significance	**	**	**

a,b: Means within columns followed by different superscripts are significantly (P<0.05) different

\*\* : significant at (P<0.01)

**Table (2): Effect of Aluminum as retanning on some physical characteristics of cattle leather**

Parameter Aluminum conc.	Thickness (mm)	Tensile strength (Kg/cm <sup>2</sup> )	Elongation (%)	Grain crack (Kg)	Grain break (Kg)
1%	2.13±0.0 <sup>c</sup>	227.37±35.9	35.4 0±1.8	7.70±0.4 <sup>b</sup>	9.13±0.3 <sup>bc</sup>
2%	1.66±0.0 <sup>b</sup>	279.68±75.1	27.30 ±1.0	7.78±0.4 <sup>b</sup>	8.95±0.2 <sup>c</sup>
3%	2.26±0.1 <sup>a</sup>	279.17±181.9	30.60 ±2.4	8.30±0.2 <sup>a</sup>	9.80±0.1 <sup>a</sup>
4%	2.09±0.1 <sup>c</sup>	215.06±37.2	38.3 ±14.6	8.10±0.3 <sup>ab</sup>	9.40±0.2 <sup>b</sup>
Significance	**	NS	NS	*	**

a,b: Means within columns followed by different superscripts are significantly (P<0.05) different

\*\* : significant at (P<0.01), \* : significant at (P<0.05), NS: Not significant

**Table 3: shrinkage temperature of garad tanned leather retanned with aluminum**

Chromium conc	shrinkage temperature
1%	70 °C
2%	71°C
3%	73°C
4%	80.1°C

Shrinkage temperature tended to increase with the increase of Al concentration. The chemical nature of collagen allows it to react with a variety of agents often resulting in its conversion to leather changes in appearance and properties that are the consequence of tanning. It is necessary to specify the conditions, because shrinking is a kinetic process and, as such can be treated thermodynamically. The relationship between shrinkage temperature and change in heat indicates that breakdown of the tanning interaction is not the cause of shrinkage. It is thought that even the weak, hydrolysable aluminum tannage is not reversed during shrinkage. The reaction, which is visible as heat shrinkage is a breakdown of the hydrogen bonding in collagen or leather; that regardless of the tanning process, the shrinkage reaction is the same <sup>[2]</sup>.

## CONCLUSION

All the results to be quite normal and this recipe for tannage by using garad with mineral aluminum reduced pollutions from used chromium tannage and introduced new cleaner technology for tanneries. It concluded that the leather produced using garad as tannage agent retannage with mineral aluminum was quite successful. It was full, soft with good physical and chemical properties. On the other side the natural color of the crust is biscuit and can be used successfully for shoe upper of natural color. It is very acceptable and can easily to compete in local and international market.

## Recommendation

Garad could be used as alternative for chromium in tannage operation to reduced environmental challenge from chromium.

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