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Optimisation of Chrome Retanning Process to the Garad (*Acacia nilotica*) Tanned Leather

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Abstract
This study aimed to reduce the environmental pollution generated by chrome (chromium III salts) that result from the tannage processes of leather. It aimed also to encourage the use of a local tannin agent which is known as garad *(Acacia nilotica)*. In Sudan, the majority of traditional artesian tanneries use garad for tanning. Some of the modern and mechanized tanneries use garad in the retannage stage. Twelve pieces pickled cattle hides were treated in pilot drum at speed of 8 rpm. In the experimental trail the pickled hides tanned with 30% garad and retanned with different offers of chrome (1%, 2%, 3%, 4%) followed by 10% garad. The chemical analysis of the leathers viz. for % moisture content, % ash content, % fat and % chrome contents were carried out for the experimental leathers. Physical testing, including thickness, tensile strength, percentage elongation at break, load at grain crack, load at grain burst and shrinkage temperature were measured. The chemical properties of leathers in all trials are found to be quite normal. The shrinkage temperature of experimental leathers for all trials found above 85.4°C and the tensile strength above 103.00 Kg/cm2.

Keywords: garad, combination tannage, shrinkage temperature, tensile strength.

Introduction

Vegetable tannin extracts are used as tanning agents to convert hide into leather in aqueous solution. An excess of vegetable tannin extracts is usually used in tanneries to ensure full penetration and reaction of tannin with collagen (Madhan *et al.*, 2005).

Tanning of animal hides produces leather, durable, flexible material that is stabilized against putrefaction. Chrome-tanned wet blue, aldehyde cross linked wet white, and vegetable tanned hides are major contributors to current leather production (Eleanor and Dvenis, 2011).

Tanning is the basic chemical reaction which can transform hide or skin into leather. Some tannages, like vegetable tanning, aldehyde tanning and metal tanning, have been used by tanners for several thousand years. The chemical principles of these tannages have been clearly revealed in the last decades and have greatly improved technologies of leather processing (Bi Shi, 2008).

Study concerns the implementation and improvement of a system that applies ultrasound technology to vegetable tanning floats in particular, the study investigated grain fineness and fixation of tannins in relation to several mechanical approaches, which included: no mechanical effect (pits), drum, ultrasound, and ultrasound plus drum (Morera *et al.*, 2010).

Leather processing is one of earliest industrial activities carried out by humans due to protection of their feet from harsh environment. Around 3000 A.D., ancient Egyptians were the first who were applying mineral tanning of leather processing. There are different methods of leather tanning (Josep *et al*., 2008 and Agrawal *et al*., 2008).

Chromium is a common pollutant introduced into natural waters due to the discharge of variety of industrial wastewaters. On the other hand, chromium based catalysts are also usually employed in various chemical processes, including selective oxidation of hydrocarbons. According to the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for total chromium is 0.05 mg/1 (Mojdeh *et al.*, 2009).

Chromium is a chemical element in the periodic table that has the symbol Cr and atomic number 24. It is steel-gray, lustrous, hard metal takes a high polish and has a high melting point. Chromium is present in the environment in several different forms. The most common forms are chromium (0), chromium (III), chromium (VI) (Mojdeh *et al.*, 2009).

Cr (III), on the other hand, is less toxic than Cr (VI) and is nearly insoluble at neutral Ph (Venitt and Levy, 1974). Cr (III) is listed as an essential element, as micronutrient, to maintain good health and helps in maintaining to normal metabolism of glucose, cholesterol, and fat in human bodies (Kimbrough *et al*., 1999). It is poisonous only at high concentration.

Large quantities of solid waste containing chromium are generated by the leather industry. In recent years the specialized literature has described protein and chromium recovery processes. The molecular weight spectrum of the recovered protein shows that for retanning purposes the average molecular weight is too low aimed to obtain an environmentally friendly protein modification process to generate high molecular weight protein to be used in the retanning step of leather wet processing (Mariliz *et al.*, 2010). The objective of this study to identify the chrome offer used for retanning the garad tanned leather to provide best properties.

Materials and Methods

Methods:

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

Processes

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 chrome 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 washing150% 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 3.8

0.4% 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

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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 chrome 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 minutes

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

The specimens for physical testing were kept in a standard atmosphere of temperature 20+_ 2°C and relative humidity 65% +_2% during 48 hours immediately preceding its use 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

Leather was cut into small pieces, to pass through a screen with circular of 4 mm. The ground material obtained from the mill called "ground leather" or "leather powder" (SLTC 1996). Total ash content, % Moisture content, % fats content and chromium oxide were 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 for tanning at constant concentration (30%). Different chrome offers (1%, 2%, 3%, 4%) were used for retanning of garad taaned leather. 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 (Covington, 1997 and Morera *et al.,* 2010).

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 (4.00-6.67%), ash (1.86-3.63%), fat (3.87-4.70) and chrome oxide content (1.38-2.90) of the produced leather fall within the normal values. The moisture content was significantly affected by the concentration of the Cr and it tended to decrease with the of Cr concentration. However, the moisture content of the leather obtained from re-tanning with 4% Cr was significantly lower than that obtained from re-tanning with all other Cr concentrations.

This study indicates that chromium as retanning agent ensures 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 when these factors change; affecting strength, permeability, and thermal stability. Retanning is a key operation in leather making to obtain leathers with some special characteristics (Keyong *et al.* 2009).

The ash content in the current study (1.86-3.63) was significantly affected by the concentration of Cr. However, all values obtained are comparable to those reported by Musa and Gasmelseed (2012). A very wide range of ash content (0.9-70%) was obtained by Haroun *et al.,* (2008). The fat % in this study (3.87-4.70) was also significantly affected by Cr concentration.

The thickness of the leather produced to the different Cr concentrations used range between 1.5-1.96 mm. Animal hides are not uniform, which mean there are big difference in thickness and type of fibril weaving existing in different areas of a hide or skin (Krysztof, 1983). All other physical characteristics determined in this study (tensile strength, elongation, grain crack, grain break and shrinkage temperature) showed high values. The Cr re-tanning improves the strength properties of the leather. The tensile strength 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 the experimental leathers gave competitive results, to produce different type of leathers (Dutta, 1999).

The percentage elongation at break load of garad tanned leathers retanned with different chrome offers (1%, 2%, 3%, 4%) 33.6%, 31.3%, 30.6% and 39.3 % 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 due to the increase the hydrothermal stability (Covington, 1997). 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 (85.4-87 °C). Shrinkage temperature tended to increase with the increase of Cr 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 thermod-ynamically. 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 chromium 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 (Covington, 1998).

Table 1: Effect of chrome retanning on some chemical characteristics of cattle leather

Parameter / *Chrome conc.*	*Moisture (%)*	*Ash (%)*	*Fat (%)*	*Chromium oxide content (%)*
1%	5.88±0.1[c]	3.43±0.2[a]	4.23±0.2[b]	1.38±0.0[d]
2%	6.10±0.1[c]	3.63±0.1[a]	3.87±0.2[c]	2.90±0.1[a]
3%	6.67±0.2[a]	1.86±0.2[c]	4.67±0.2[a]	2.10±0.1[c]
4%	4.00±02[b]	2.66±0.[1]	4.70±0.2[a]	2.50±0.0[b]
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 chrome retanning on some physical characteristics of cattle leather

Parameter Chrome conc.	*Thickness (mm)*	*Tensile strength (kg/cm2)*	*Elongation%*	*Grain crack (Kg)*	*Grain break (Kg)*
1%	1.68±0.16[b]	103.00±18.4[c]	33.6±4.8[ab]	8.28±0.4[a]	9.50±0.1
2%	1.63±0.16[bc]	159.00±11.96[b]	31.3±1.4[b]	6.18±0.8[b]	8.60±1.5
3%	1.96±0.00[a]	171.00±40.4[a]	30.6±1.8[b]	5.78±0.9[b]	8.75±0.5
4%	1.50±0.00[c]	185.75±76.4[ab]	39.3±7.2[a]	7.85±0.5[a]	9.35±0.2
Significance	**	**	*	**	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 chromium

Chromium concentration	Shrinkage temperature
1%	85.4 0°C
2%	86.00 °C
3%	86.40 °C
4%	87.00 °C

Conclusion

The experimental leathers in this study gave good results and this recipe for tannage by using garad with mineral chromium reduced pollution and introduced new cleaner technology for tanneries, it concluded that the leather tanned with garad and retanned with chrome was quite successful. The experimental 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. The experimental leather is very acceptable, and can easily to compete in local and international market.

Recommendation

It is necessary to carry out more studies to compare economic effectiveness between this recipe and the tanning by using chromium.

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ضبط عمليات اعادة الدباغة بالكروم للجلود المدبوغة بالقرض

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المستخلص

اهمية هذه الدراسة التقليل من التلوث البيئي الناتج من استخدام الكروم وتشجيع استخدام المادة الدابغة المحلية في السودان. معظم المدابغ المحلية تستخدم القرض في الدباغة بعض المدابغ الحديثة تستخدم القرض في اعادة الدباغة، 12 قطعة جلد بقري عولجت في برميل سرعته 8 دورة في الدقيقة. في كل التجارب جلود محنطة دبغت ب30% قرض وفي اعادة الدباغة نسب مختلفة من الكروم (1%، 2%، 3%، 4%) واتبعت ب 10% قرض. الجلود المنتجة اجريت لها الاختبارات الكيمائية وهي نسبة الرطوبة، نسبة الرماد نسبة الدهن ونسبة محتوى الكروم والاختبارات الفيزيائية وهي السمك، قوة الشد، الاستطالة. كل الجلود اعطت نتائج كيمائية طبيعية واعطت درجة انكماش اعلى من 85.4 درجة مئوية وقوة شد اعلى من 103كلجم لكل سنتميتر مربع.