



Chromium combination tannage of rural and minimal tanned crusts

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Abstract

Chrome tanning gives the tanned hide/ skins many good properties such as degree of fullness ,softness , resilience standard shrinkage temperature . The study aims to make use of this by a ppling combination tannage. This was done by treating the traditionally vegetable tanned leathers with semi chrome tanning .

Vegetable tannin are a group of polyphenolic compounds extracted from plants and used tannage . The infusion and subsequent binding of vegetable tannins to animal hides or skins usually results in increased shrinkage temperature from the range 60-65c for an untanned hide skin to about 80c . The mechanism through which the vegetable tannins raise the shrinkage temperature of leather by the potential of forming multiple hydrogen bonds , it is considerable that they can cross -link collagen molecules and there by stabilize the fibrillary network of the skin .Nevertheless , high shrinkage temperature is requiring by shoe upper manufactures to be 100c . Hence a combination tannage of chrome – vegetable will improve the shrinkage temperature of the vegetable tannins and the feel of fullness of the chrome leather . Acacia nilotica tannins is used as retanning or pretanning agent for producing minimal crusts which are further semi chrome to give the properties of chrome – vegetable combination tannage . Third sheep skins were minimally tanned and processed until finished leathers . The leather produced was analyzed for physical and chemical properties and showed good degree of fullness , softness and resilience . To encourage the rural tanner and promote their process and production third sheep skins which were tanned by rural process , stripped with soda ash and semi-chromed . The crusts were further processed up to finishing .The finished leather s were analyzed and showed good results . To help the rural tanners to increase their production and to cope with clean technology . A small experimental drum is designed and it can be easily put into service by the rural tanners with very low cost .

The objectives:

- Development of a simplified semimechanzed vegetable- chrome tannage for small scale artisiantanners .
- Development of minimal tannage process for rural tanners and rationalize their recipes.-
- Improvement of the quality of rural- minimal tanned crust through semichroming tanned.

1.1Introduction

Tanning is the process of converting raw hides or skins into leather . Hides and skins have the ability to absorb tannic acid and other chemicals that prevent them from decaying , make them resistant to wetting and keep them supple and durable

Leather a common place item found in every day life is a product obtained by tanning skins and hides by several methods. The origin of leather begins with the origin of man kind and civilization . It has been said that the progress of civilization has coincided with the development of leather (3).

Since the leather industry required relatively concentrated sources of tannins, much technical attention was devoted to analysis of plant materials for tanning agent content .The origin of the art of vegetable tanning is hidden in the mists of antiquity .

In prehistoric times it was discovered that the properties of raw hides and skins under go a radical change when they are brought into contact with the aqueous extract of certain roots and herbs . The active vegetable principle is capable of combining with protein to convert it into an putrescible material is known as tannin .

Tannins material used by the tanners obtained from various plants in the form of barks , wood , fruits , leaves ,tuiqs ,roots and pods . The tannin which appear to be by- products of the metabolism of the plants are water soluble complex organic compounds (5) .

The most important organic tanning agents are the vegetable tannins present in tanning liquors . They are prepared from contain parts of plants by aqueous extraction .

Their tanning power has been appreciated for a long time and Babylonian texts have recorded their us .

Sudan is rich endowed with indigenous tanning materials . Some of these such as garad pods (acacia nilotica sub Spnilotica) is used extensively in Sudan by the rural tanners as sunt is abundant in the Sudan . It grows along water courses permanent or seasonal , all over the northern parts of Sudan and along white Nile north of jebelein . The rain constituent making the garad tannin is gallic acid esterified with flavonoid compounds .

Garad tannin is reported to contain chebulinic acid, gallic acid and high sugar content which are common in hydrolysabl tanning materials(2). Garad tannins are mixed tannins consisting of catechol and pynogallol tannins which are phenolic compounds of the types(2).



Previous works on the use of garad tannins were limited to the production of vegetable tanned crust (Similar to East Indian crust) and its use as pretanning agent for the production of sole leather(2). Spraydried extract blend of garad husk and sunt bark in the ratio of 1:1, containing 45=45% tannin, was found to produce good quality sole leather comparable with that produced with mimosa extract.

This blend extract was proposed as substitute for imported extract(14).

Furthermore Ayoub(1985, 1986) and basher et. Al(1987) etemons traded thaspray- dried powder of the aqueous autonc and alcohol extract from the pods and stem bark of acacia niloticasubssp.

Nilotica, to mentosa and as stringency were promising vegetable moleusciciders and algicides.

The garad material principle uses in rural tanning (minimal tanning). Almost potential tanning, retanning and molluscicidal and algicidal material continuing efforts towards large scale production of high quality tannin are required – it is widely accepted that industrialization is the key route to poverty eradication, especially in countries like Sudan (1).

Where a high percentage of the population more than 70%) stile live in rural are as with a similar percentage of them engaged in agriculture and most of them earning less than per day- Trickle-down benefits from generalized economic growth have not substantially altered this situation(1).

It seems indisputable that the need is for rural industrialization to create sustainable employment in the non farm sectors in rural areas.

In the vegetable tanning process , the concentration of the tanning materials starts out low and is gradually increased as the tannage proceeds It usually takes 3 weeks for the tanning material to penetrate to the center of the hide .

The traditional method of vegetable tanning was slow and expensive, furthermore , did not always give the properties desired in the leather – not only was there some time too much firmness to the leather , but frequently the colors of the leather was not as pale or as uniform as it can be made by the use of more modern methods of tanning.

Vegetable tanned leather products has a low thermal stability and brown color rural tanned leather products is so hard , with a low shrinkage temperature and its not good in quality for use of unsystematically methods and no control of mechanical action .pH control of the contents of acids and salts . This study may contribute upgrade the rural tanning by use of short recipe and partial modernization of local materials to do this work to assist the artisan to produce good quality leathers .

The upgrading of vegetable tanned leather crust may be achieved by combination tanning (vegetable- chrome tan). Chrome- tanned leather tends to be softer and more pliable than vegetable – tanned leather, has higher thermal stability, is very stable in water, and takes less time to produce than vegetable- tanned leather.

Almost all leather made from lighter – weight cattle hides and from the skin of sheep, lambs, goats and pigs is chrome tanned. The steps of the process(soaking, fleshing, liming, deliming, dehairing and bating) the drying / finishing steps are essentially the same as in vegetable tanning.

However, in chrome tanning, the additional process of re- tanning, dyeing, and fat liquoring usually performed to produce usable leathers and preliminary decreasing step maybe necessary when using skins, such as sheep skin. (4, 6, 7).

The results of this study through the analysis (physical and chemical)indicated that leather produced is good quality, and a successful upgrading of the rural tan, that it can assess the rural tanners to increase their economic revenue and decrease the efforts of traditional minimal tannage process.

1-2 Material and methods :-

60 samples of skins were processed , 30 pieces were of goat skins in the crust conditions and 30 were sheep skins pickled .

1- 2Methods :-

1-2-1Chemical analysis :-

Sampling location for skins :-

The pieces for chemical analysis were cut from official sampling position

Preparation of sample :-

Leather was cut into small pieces , to pass through a screen with circular preformation of 4 mm . The pieces , were thoroughly mixed and brought to state of homogeneity by keeping them in a closed container overnight . After determining their moisture content , they were stored in a glass jar for further analysis (10).

determination of moisture, determination of fat content , determination of ash content, determination of water soluble, determination of hide / skin substance and determination of chromic oxide in leather.

1-2-1-1 Determiation of chromic oxide in leather by wet oxidation



1g of semi chrome leather (from 2 samples) was weighed into a 500 ml conical flask.

5 ml add concentrated nitric acid followed by 15 ml of oxidizing mixture (prechloric acid + sulfuric acid 2:1) were added . The mixture was heated in fume cupboard with the fan on until it turned orange and the heating was continued for 1 minute more .

After cooling , approximately 150 ml of cold distilled water and few anti bumping granules were added , then the solution was heated to boiling for 10 minutes , to remove any free chlorine .

The solution was allowed to cool and diluted to 250 ml with distilled water in volumetric flask . 50 ml of the solution were pipette in conical flasks and 10 ml of 10% potassium iodide solution was added to each flask , using measuring cylinder , then the flasks were stopped and placed into the dark for 10 minutes . Starch indicator , (1 ml) was added to flask , then titrated with 0.1 mol dm⁻³ sodium thiosulphate solution until a pale violet color is reached (9) .

Calculation :-

Chromic oxide (Cr₂O₃) , % = $T1 \times 0.00253 \times 100 / M0$

Where:

T1 = volume of sodium thiosulphate that used in the titration .

1 ml 0.1 N titration = 0.00253g Cr₂O₃

M0 = mass of dry sample of chromium leather .

After that determined of a cid combined with chromium , determined the tannin absorbable by hide powder and determination of minerals contents.

1-2-1-2 Determination of minerals content:-

Mineral contents were determined by atomic absorption spectroscopy (Agilent ,) perkin Elmer A.A.S Device model GBC 932 ,U.S.A.1996).

The Ash obtained from dry a shing was treated with 10 ml of conc .hydrochloric acid , dissolved and cooled then transferred to a 200 ml volumetric flask . Distilled water was added till the mark , and mixture was shaken well . Elements were then measured by A.A.S .

1-2-2 Physical Analysis

Preparation of sample :-

The pieces of physical tests were cut from the official sampling position (HGJK) and from shoulder .

Conditioning :-

The specimens for physical testing were kept in standard a atmosphere of temperature 20 +2% and relative humidity 65 %+ 2 % during 48 hours immediately preceding their use in attest . After that the physical testing was done like :-

•Measurement of thickness , measurement of tensile strength and percentage elongation.

Measurement of distension and strength of grain by ball Burst test:

Lastometer was used , it provided with :

i- A clamp for holding securely the rim of circular flat disc of leather , while leaving the central portion of the disc free to move . The clam holds the clamped area of disc . Stationary when any load up to 80 kg is applied to it scentre . The diameter of free is 0.25 mm .

ii- A mechanism for thrusting a steel ball , with rotation , against the center of the flesh side of leather disc , and measuring the load applied, the ball diameter is 60 .25 mm , and the accuracy of load measuring mechanism shall be such that the load at grain crack and burst of the specimen is measured with and error not exceeding 3 % .

Preparation of specimens to the dimensions required for calming them in the apparatus :-

Procedure :-

1-The specimen was clamed in the instrument with its flesh surface adjacent to the ball , and its grain surface flat .

2-The distention , is increase and the grain surface watched for the occurrence of cracks , and corresponding values at the burst were recorded if the leather disc burst before the maximum load is reached (JLTC , 1960) .

1-2-2 Boiling test:

The semi- chrome tanning process is usually considered to be completed when a piece of tanned leather does not shrink in boiling water for three to five minutes. A sample was cut from the thickest part of the tanned hide or skin, smoothed out on a piece of wooden board and its boundaries outlined with a pencil



The sample was then placed in a bowl of water kept at boiling point for three minutes.

The sample was then taken out. Cooled, smoothed out again and the shrinkage noted, by the contraction, of any of the boundary lines.

The boiling test and the shrinkage temperature for quite a number of these leathers as low as 90C or round about

Principle:-

A sample of the leather under test is rubbed with revolving felt pad and the number of revolution of the pad required to produce certain effect is measured.

1-2-3 Effect of leather: wet rubbing.

A procedure:-

a) The standard felt pads were immersed in boiling water, allowed to cool at room temperature. The weight of each wet pads was adjusted by squeezing out water or adding cold water until it lied between 2- 3g. immediately before using. Pads should not be kept in water for more than 24h.

b) The leather test pieces were clamped on the specimen platform of the machine and the smaller weight was placed on the platform at the top of the vertical shaft, a wet felt pad was pressed on to the three spikes at the bottom of the vertical shaft. The pad was lowered on the test piece, and immediately the motor was switched on the motor switched off after eight revolutions of the pad, and was raised.

C) The test pieces were moved away from the area below the pad so that the pad could be changed with a new one, and the test was repeated to give new revolutions. This procedure was repeated and gave successively 32, 64, 128, 256, and 1024 revolutions.

d) The leather was dried and arranged with the test areas in sequence.

e) When it was necessary to restore the appearance of the leather , a little emulsion applied .

f) The test areas , allowed to dry thoroughly and polished with a clean soft cloth .

g) The test areas where examined , and it was decided which was the first in numerical order of rubs , to show in its most affected part (normally the periphery) contrast of appearance with the surrounding leather equivalent to or greater than that given by grade 4 on the standard grey scale for assessing change in color .

h) The contrast between the tested area which has been given 1024 revolution , of the pad , and the surrounding leather , was assessed by using the grey scale .

(11) – The result was expressed as follow:-

1- Number of revolutions required to cause a contrast of grade 4 above) . The nature of change was description.

2-Number of revolution required to cause, a contrast of grade, if this is 1024 or less) .

1-2-4 Effect on leather: dry rubbing

Procedure:-

The leather test pieces were clamped on the specimen platform of the machine and the larger weight was placed on platform at the top of the vertical shaft.

One of the standard felt pads was pressed onto the three spikes at the bottom of the vertical shaft, the pad was lowered onto the test piece and the motor switch on.

ii) The test pieces were removed form below the pad so that could be pad changed for a new one and the test was repeated giving , 64 revolutions .

The procedure was repeated and giving successively 128 , 256 ,512 , and 1024 revolutions and if desired 2048revolutions also .

iii) The tested areas were arranged in sequence and polished slightly using a clean soft cloth and a little carnauba in emulsion , if the appearance of the leather was necessary to restore .

iv) The tested areas were examined , and it was decided which was the first in numerical order of rubs , to show in its most affected part (normally the periphery) a contrast of appearance with the surrounding leather , equivalent to or greater than that given by grad 4 the standard grey scale for assessing change in color .

The results were expressed in the same as the results of wet rubs.

Followed by:-



Table (1-1) iron content in garad pods by atomic absorption spectroscopy

Blue Nile garad pods	West of Sudan garad pods
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sample	Conc,µg/ml	Conc,µg/ml
seeds	3.951	3.098
Grain pods	1.275	0.923
husk	2.102	1.147

Table (1-2) garad constituents (Blue Nile):

Determined	Result
Total solids	33.38%
Total soluble	33.10%
Non tannins	8.20%
tannins	25.40%



**Table (1-3) chemical properties of leathers produced by different techniques:-
Chrome powder of 24.6% Cr₂O₃ and 33% basicity is use**

Numbers Constituent%	I	II	III	IV
	Moisture%	4.7	7	8.1
Ash%	2.8	2.3	5.4	1.8
Fat%	0.9	2.8	2.7	3.5
Water soluble%	18.8	4.7	7.2	3
Cr ₂ O ₃ in leather%	AN	AN	1.6	2
Nitrogen%	5.9	6.7	5.6	7.12
Hide substance%	33.3	37.3	31.4	40
Cr ₂ O ₃ in liquor%	AN	AN	2.6	2.14
Fixed tannins%	33.5	38.3	35.3	42

- I Crust of rural tannage**
II Crust of minimal tannage.
III semi –chromed leather of rural tannage.
IV semi –chromed leather of minimal tannage.
AN not applied.

Table (1-4) Physical properties of leathers produced by different techniques:-

Types	Thickness Cm	Tensile Strength Kg/Cm ²	Elongation%	Load at break Kg
I	0.128	69.36	40%	17.77
II	0.11	111	67%	24.4
III	0.10	100	67%	20
IV	0.0837	146.27	80%	24.4



Table (1-5) Physical properties of crust leathers at various temps:-

Sample Number	I	II	III	IV
Temperature °C	45	50	75	85 - 90
Load at crack Kg	11.2	24.9	18.0	20
Load at burst Kg	23.1	44.3	24	26.4
Felxometer	20.000	25.000	43.000	60.000

I: Crust of rural tannage.

II: Crust of minimal tannage.

III: semi –chromed leather of rural tannage.

IV: semi –chromed leather of minimal tannage.

Table (1-6) Wet and Dry rub tests for finished Nappa:

type	Wet rub/rpm	Dry rub / rpm
1/ finished nappa from semi-chromed leather of rural tannage.	412	730
2/ finished nappa from semi-chromed leather of minimal tannage.	510	960



DISCUSSIONS:

The samples used are:

I-Crust from rural tanneries: , this was treated by the traditional method of rural garadtannage. It consumed a lot of tanning material and time.

II-Minimal tanned Crust :This a rapid tannage for which the pelt is pickled and tanned in a short float garad and salt. It usually takes almost ¼ of the amount used in rural tannage. It is less expensive and gives a good filling property to the leather.

III-Semi –chromed rural tanned crust: This is made by stripping the excess loose and loosely fixed garad tan by sodium carbonate , the PH is adjusted to 2.8 – 3.0 by an acid and then chrome –tanned.

IV-Semi –chromed minimal –tanned crust : this is made by light stripping with sodium carbonate , the PH is adjusted and Semi –chromed.

Both crust (III and IV) were analysed for physical and chemical properties.

The crusts were further processed to produce suede and nappa leathers.

Tables (1) to (6) indicate the results of analysis.

The iron content which exists in garad pods has a considerable effect on the color and durability of the tanned leather .There are two types of garad pods which are used , the Blue Nile source pods and the west of Sudan source ones , each has different iron content as shown in Table (1) . The iron content must be removed before or during tannage . The removal of iron can be carried out by ion –exchange treatment or it can be masked by a chelating agent .The chelating agent such as oxalic acid will mash the iron and render it in reactive . The latter method is easy and practical , it has been practiced in modern tanneries since the seventies . Hence ,the same method of oxalic acid treatment was adopted in this study and showed no effect of iron as indicated by the physical and chemical analysis. Table (2) shows the analysis of garadcontents , from this table ,it is observed that the garad pods have a high tannin content of greater than 25% with a total soluble of greater than 33% and this is why garad powder can be used for pre tanning and combination tannage.

Nevertheless , the best method is to make a spray dried powder of garad tannins which can reach a concentration , as high as greater than 60% In future this can be important and needs to be put into application.

Using garad grain powder for tannage and combination tannage, four sets of samples of different processes were applied. A purely garad –tanned crust from rural tanneries , a minimal garadtannage crust , and semi –chromed rural – tanned crusts and semi –chromed minimal tanned crusts were investigated.

Each sample of the semi –chromed leathers was analyzed for chemical and physical properties .The results are shown in Tables number (3,4,5,6) .

The leather produced is of good quality having the filling effect of vegetable tannage and the strength of chrome mineral tannage.

From the results above analysis ,garad tan can be used in modern tanneries in minimal tannage process for export and as a very effective pretanning agent .This will replace the expensive imported syntans, the same can be applied in rural tannage. It is observed in this study that the semi –chromed rural –tanned leather will be a very good supply for the mechanized tanneries to produce suede and nappaleathers .

But ,it is suggested in this study that the rural tanneries must be semi-mechanized .

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