

# Chrome-free Tannage: Suede Garment Leathers from Rural Vegetable Sheep Crust Leathers

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**ABSTRACT:** Worldwide research is being focused on chrome-free tanning systems. Many studies based on less chrome and chrome-less technologies have emerged in the recent past. The tannin molecules in vegetable tanned leathers form multiple hydrogen bonds with collagen and create a polyphenolic tanning matrix. The hydrothermal stability of vegetable tanned leather is in the range of 70-85°C. By retanning of vegetable tanned leather with metals the shrinkage temperature (Ts) can be elevated considerably in a process that is commonly known as semi-metal tanning. Semi-metal tanning systems have gained importance in recent times as an alternative for chrome tanning. In this study, an attempt has been made to manufacture of semi-alum garment leathers from sheep rural garad tanned crust leathers. Sheep rural garad tanned crust leathers carefully sorted for size, substance, and grain quality, so that the customers' requirements can be met accurately. The selected crust leathers followed the subsequent processing, viz, stripping, bleaching, retannage with aluminium sulphate prepared solution, neutralization, dyeing, fatliquoring, drying and finishing. Full chrome tanned garment leathers from sheep skins used as control leathers. The physical and chemical characteristics of experimental leathers are comparable to control leathers. The experimental trial resulted in very soft and flexible leathers with high tensile strength. However, the stripped rural garad tanned leather retanned with 2% Al<sub>2</sub>O<sub>3</sub>; resulted in shrinkage temperature of 102°C. The experimental trial resulted in leathers with good organoleptic and strength properties. The semi-alum tanning system provides significant reduction in the discharge of total dissolved solids in the wastewater. The work presented in this paper established the use of semi-alum tanning system as an effective alternative cleaner tanning methodology.

**KEYWORDS:** Garad, Semi-alum, Stripping, Shrinkage temperature, Crust leather

## I. INTRODUCTION

The skins of all animals have, in their time, been used for garments. However, because this is the most worthwhile use for them, most clothing leathers are now made from the skins of woolled sheep or lambs killed for the meat trade. Other sheepskins, such as those of hair sheep, tanned primarily for glove leather, are also used for clothing. Much clothing leather is made from East Indian and other vegetable tanned sheep and goat skins after a chrome retannage. Both grain and flesh splits from bovines are also used. The latter often provide a particularly inexpensive raw material, but in all these cases the original tannage is not specifically designed for clothing leathers [1]. The substance of garment leather must be uniform and varies between 0.5- 0.8 mm (suede garment) or between 0.6-0.8 mm (grain garment). The substances of lower grades are sometimes kept between 0.8-1.0 mm. The garment leathers must be of light weight, soft and flexible with some amount of 'spring' but should never be too stretchy to make the garment de-shaped during wear. The other desirable properties of clothing leathers are a good drape, uniform appearance, low density and a satisfactory tear-strength [2].

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Leather tanning is dominated by the use of chromium (III) salts, because it gives leather unmatched hydrothermal stability and excellent organoleptic properties [3]. However, chrome tanning has some negative attributes, posing serious challenges to our continued reliance on it. As a limited resource, chromium (VI) is a well-known carcinogen, but chromium (III) is considered as non-toxic [4]. The chromium (III) existing in leather might be transformed into chromium (VI) in some extreme conditions [5]. Therefore, the chrome remaining in wastewater and the solid wastes may be harmful to the environment. Nevertheless, the one property, which chromium has not been able to provide is fullness, as chrome tanning alone is known to produce leathers which are empty in nature [6].

Vegetable tanning has been considered as a suitable ecofriendly option to replace chromium. However, vegetable tanning has some shortcomings such as the fullness of vegetable leathers which prevents its use for some end products. Vegetable tannins are also difficult to biodegrade [7]. Amongst mineral tanning agents, aluminium, [8] titanium, [9] iron, [10] zirconium [11] have been explored for their solo tanning potential but each one has associated disadvantages. Iron tanned leathers darken during ageing, zirconium salts are high cost items and the hydrothermal stability of aluminium tanned leathers is low compared to chrome tanned. Combination tannages are thus being considered as suitable alternatives for chrome-free tanning systems. In vegetable tanned leathers, tannin molecules form multiple hydrogen bonds with collagen and create a polyphenolic tanning matrix. The shrinkage temperature ( $T_s$ ) of vegetable tanned leather is in the range of 70-85°C [12]. By retanning with metals such as aluminium the  $T_s$  of vegetable tanned leather can be elevated considerably in a process that is commonly known as semi-alum tanning. Similarly, retanning of vegetable tanned leather with metal salts has been referred to as semi-metal tanning [13].

Semi-chrome leather is used as substitute for chromium tanned goatskin, particularly when a heavier substance is required, for example, for unlined casual footwear and slippers. The classical raw material for this leather is East Indian goatskin from India exported in the lightly vegetable tanned crust state. Alternative and expanding supplies are available from Pakistan, East and West Africa, and the Middle Eastern countries. The quality of these leathers has improved recently as far as the process in itself is concerned; but commercial factors affect their qualities, which suffer from the fact that these skins are mainly produced by small tanners, who cannot afford the high prices paid by the larger chrome tanners for their raw skins. These leathers are sold by weight in the crust, so that they are often adulterated with Epsom salts (magnesium sulphate), colloidal earths, added fats. The incidence of faults attributable to the presence of large quantities of natural and added fats in increasing, particularly in suede leathers, so that solvent degreasing of the crust goatskins is being carried out by some dressers [14]. Semi-chrome leather is first vegetable tanned and subsequently retanned with chrome salts. The accepted model of the principal interaction in semi-metal tanning is based on complexation of metal ion by the metal-polyphenol (Fig. 1). The chelated complexation of the metal centre creates crosslinks in the polyphenolic tanning matrix resulting in the formation of an extended supramolecular tanning matrix around the collagen. Subsequently, the shrinkage temperature is increased considerably [12].

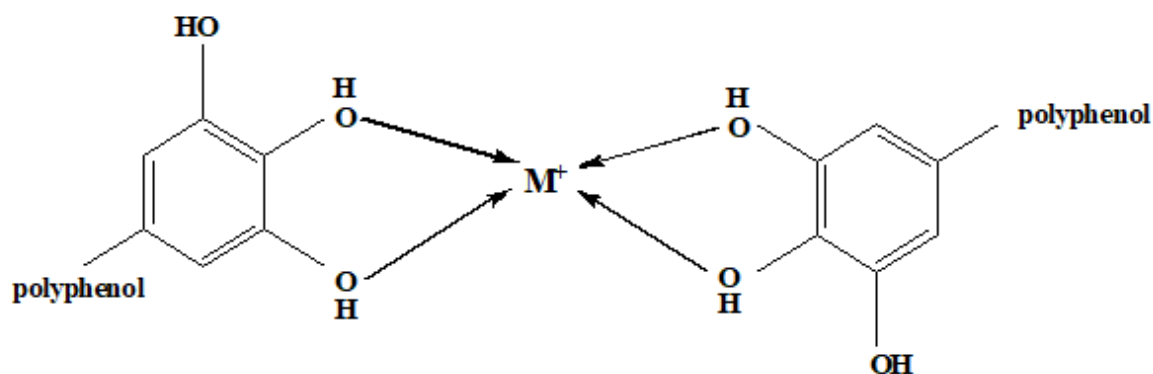


Fig. 1: Basis of the semi-metal tanning reaction (Covington, 2009)

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*Acacia nilotica* pods which are widely used by the industry in both the rural and mechanized sectors has been given different names by different tribes viz. Bagaruwa or Gabaruwa (Hausa in Negeria) and Sunt-garad (Sudan) [15]. Sudan has various indigenous tanning materials. Some of these, such as Garad pods (*Acacia nilotica* sub. sp. nilotica) and Talh bark (*Acacia seyal*) are used extensively in the Sudan by rural tanners. The tannin content of garad pods is fairly high and amounts to approximately 30% of the total weight, soluble nontans are nearly 20%, while moisture and insolubles make up the remainder. The main constituent of the garad tannin is presumably leucocyanidin gallate i.e. gallic acid esterified with a flavanoid. Garad tannin is reported to contain chebulinic acid, gallic acid and to have a high sugar content, factors which are common in hydrolysable tanning materials. Garad tannins are therefore mixed tannins i.e. containing condensed tannins as well as hydrolysable tannins containing gallic acid esterified with glucose [16]. The basic objective of this study is to develop a chrome free tanning system based on a semi-metal from rural vegetable tanned crust leathers for production of garment leather.

## II. MATERIALS AND METHODS

### Materials

Sheep rural garad tanned crust leathers without any grain defects have been taken for tanning trials. The selected leathers dipped in water, piled for several hours to condition uniformly, and then shaved at thickness 0.8 mm. The usual process consists of wetting back, stripping, bleaching, retanning with aluminium salt solution, neutralization, dyeing, fatliquoring, drying, and finishing. The leathers are weight after shaving. The aim of stripping is a light detannage in order to obtain increased uptake of aluminium sulphate salts. Chemicals used for post tanning processes have been of commercial grade. Chemicals used for the analysis of spent liquor have been of analytical reagents.

### Basic Aluminum Sulphate Solution

A known amount of Aluminum sulphate has been taken in a beaker and 150% of water (% based on the weight of Aluminum sulphate) has been added and the solution stirred for 15-20 minutes, subsequently required amount of ligand (sodium citrate and sodium tartrate) have been added and stirring has been continued for 45 min followed by slow addition of sodium carbonate until the pH has been raised to 3.5. For 0.5M of Aluminum sulphate 0.1M of ligand has been added.

### Methods

#### Procedure for Processing the Garment Leathers

The experimental process for rural garad tanned crust leathers is given in Table 1. The amount of aluminum sulphate used for the experimental trial is 2%  $Al_2O_3$ . The control process for full chrome garment leather from Sheep skins using 8% basic chromium sulphate (BCS), is given in Table 2. The post tanning process as mentioned in Table 3 has been followed for experimental and control leathers.

#### Shrinkage Temperature

The shrinkage temperature of control and experimental leathers has been determined using Theis shrinkage tester [17].  $2 \times 0.5 \text{ cm}^2$  piece of tanned leather cut from the official sampling position has been clamped between the jaws of the clamp and has been immersed in solution containing 3:1 glycerol: water mixture. The solution has been continuously stirred using mechanical stirrer attached to the shrinkage tester. The temperature of the solution has been gradually increased and the temperature at which the sample shrinks has been measured as the shrinkage temperature of the leathers.

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**Table 1 Recipe of the Experimental Trial for Semi-alum Leathers from Sheep Rural Garad Tanned Crust Leathers**

Process	%	Chemicals	Duration (min)	Remarks
Washing	100	water	15	
Stripping	100	Water Sodium bicarbonate	60	Single feed, washed well after stripping
Bleaching	100	Water		
	1	Oxalic acid	60	1 feed, pH should be 3.5 drain 50% of bath
Semi alum tanning	2	Al <sub>2</sub> O <sub>3</sub> (prepared Aluminium sulphate solution)	90	Check for penetration in cross section
Basification	0.75	Sodium bicarbonate	3 × 15	Check the pH to be 4. Drain the bath and pile overnight. Next day sammed and shaved to 0.8 mm. The shaved weight noted.

### Physical Testing

The leathers were sampled as per IULTCS methods [18] and conditioned at 80±4°F /65±2 % R.H. for 48 hrs. Tensile strength, elongation, tear strength and grain crack were investigated as per standard procedures [19-21]. Each value reported is an average of four tests (2 along the backbone, 2 across the backbone).

### Organoleptic Properties

Experimental and control crust leathers have also been assessed for softness, fullness, grain smoothness, grain tightness (break), general appearance and dye uniformity by hand and visual examination. Three experienced tanners rated the leathers on a scale of 0-10 points for each functional property, where higher values indicate better property of leathers.

### Analysis of Spent Tan Liquor

The spent liquor from control and experimental tanning processing were collected, filtered and analyzed for chemical oxygen demand (COD), Biochemical oxygen demand (BOD<sub>5</sub>), and total Dissolve solids (TDS) as per standard procedures [22].

### Chemical Analysis

The chemical analysis of the leathers viz. for total ash content, % moisture, % oils and fats, % water soluble, % hide substance, % insoluble ash and degree of tannage were carried out for control and experimental leathers as per standard procedures [23]. ( Triplicates were carried out for each sample and the average values are reported.

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**Table 2: Recipe of the Control Trial for Full Chrome Garment Leather from Sheep Skins**

Process	%	Product	Duration (min)	Remarks
Soaking	200	Water		
Painting	10	Water		
	2	Sodium sulphide		
	4	Lime		Apply the paste on to the flesh side and pile over night. Next day unhairing.
Reliming	100	Water		
	8	Lime		Dip the unhaird skins in this lime liquor for 2 days. Then do fleshing
Deliming and Bating	100	Water		
	1	Ammonium Chloride	60	
	0.25	Bating Agent	60	pH 8-8.5
Pickling	100	Water		
	10	Salt	10	<sup>o</sup> Be 6-7
	0.2	Formic Acid		
	1	Sulphuric Acid	3x15+45	pH 2.8-3 , Two day ageing
Chrome tanning	50	Pickle float		
	50	water		
	8	Basic Chromium Sulphate	90	
Basification	1	Sodium formate	20	
	1	Sodium bicarbonate	3x15+45	Check the pH to be 4. Drain the bath and pile overnight. Next day sammed and shaved to 0.8 mm. The shaved weight noted.

**Table 3: Recipe of Post-tanning Process for Control and Experimental Leathers**

Process	%	Chemicals	Duration (min)	Remarks
Washing	200	Water	10	
Neutralization	0.75	Sodium bicarbonate	3 × 15	pH: 5-5.5
Retannage	100	Water		
	7	Syantn	120	
Fatliquoring	14	Synthetic fatliquor	90	
Dyeing	3	Acid dye brown	30	
Fixing	1	Formic acid	3 × 10 + 30	pH 3.5

\* - % chemical offer is based on shaved weight of the tanned leather

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### III. RESULTS AND DISCUSSION

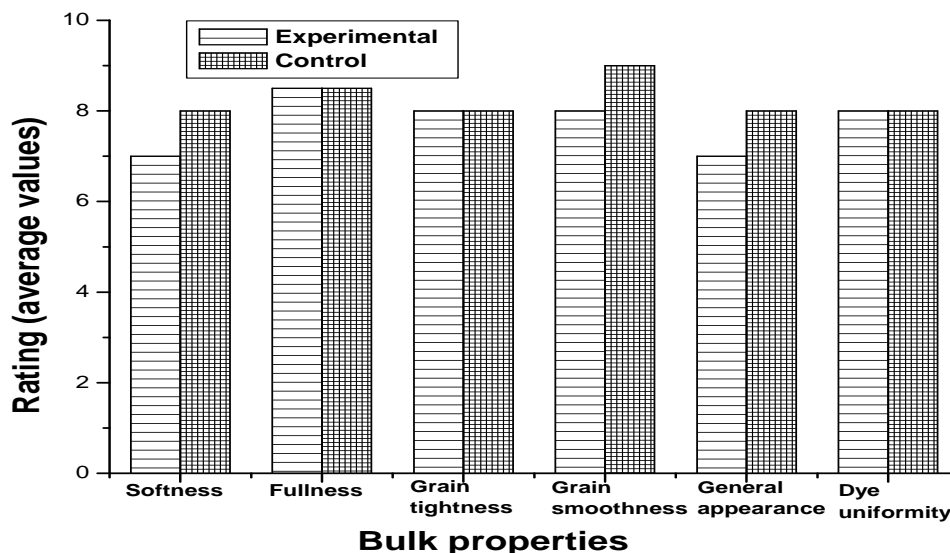
Experimental leathers treated with 2% Al<sub>2</sub>O<sub>3</sub> resulted in garment leathers with higher temperature. Experimental trial resulted in leathers with shrinkage temperature 102°C, whereas control tanning using full chrome resulted in a shrinkage temperature of 105°C. (Table 4)

**Table 4: Shrinkage Temperature of Control and Experimental Tanning Processes**

Experiment	Shrinkage temperature (°C)
Semi-alum (control )	102 ± 1
Full chrome	105 ± 0.5

#### Organoleptic Properties of Crust Leathers for Experimental and Control

Crust leather from both control and experimental processes has been evaluated for various bulk properties by hand and visual evaluation. The average of the rating for the leathers corresponding to experiment has been calculated for each functional property and is given in Fig. 2. Higher numbers indicate better property. The experimental leathers exhibit similar or comparable softness and fullness compared to control leathers. Grain smoothness and general appearance though not higher, are comparable to that of conventionally processed leathers. Overall the performance of both control and experimental leathers are similar.



**Fig. 2 Graphical Representation of Organoleptic Properties of the Experimental and Control leather**

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### Physical Strength Characteristics of Crust Leathers for Experimental and Control

It is essential to study the influence of the tanning system on the strength properties of leathers. The physical strength measurements viz., tensile strength, elongation, tear strength, load at grain crack and distension at grain crack were carried out for the control and experimental crust leathers and the data is given in Table 5. From the table it is observed that full chrome and semi alum crusts leathers showed improved strength properties on par with the standard range for garment leathers.

**Table 5: Physical Strength Characteristics of Experimental and Control Crust Leathers**

Parameter	Experimental (semi-alum)	Control (full chrome )
Tensile strength (Kg/cm <sup>2</sup> )	195±20	205±5
Elongation at break (%)	52±0.75	56±1.48
Tear strength (Kg/cm)	49±2	54±5
Load at grain crack (Kg)	25±1	21±1
Distention at grain crack (mm)	12±0.5	13±0.5

### Analysis of Spent Liquor

The COD, BOD<sub>5</sub> and TDS of the spent liquor for both experimental and control trials were determined and are given in Table 6. From the table it is observed that the COD, BOD<sub>5</sub> and TDS of the spent liquor processed using semi-alum tanning system (experimental) are lower than control tanning trial.

**Table 6: Characteristic of Spent Liquor for Experimental and Control**

Experiment	COD(mg/l)	BOD <sub>5</sub> (mg/l)	TDS (mg/l)
Semi-alum (Experimental)	111400±2000	14400±1500	64400±2000
Full chrome (control)	128600±2850	25200±1050	92160±1500

### Chemical Analysis of the Crust Leather

The chemical analysis of crust leathers from control and experimental tanning trials are given in Table 7. The chemical analysis data for the experimental leathers is comparable to the control leathers. However, the water soluble matter for the control leathers is more than the experimental leathers.

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**Table 7: Chemical Analysis of Crust Leather of Experimental and Control**

Parameter	Experimental (semi-alum)	Control (full chrome )
Moisture %	13.20	12.50
Total ash content %	2.20	2.80
Fats and oils %	3.10	6.30
Water soluble matter %	3.60	4.50
Hide substance %	51	48
Insoluble ash %	1.4	1.45
Degree of tannage %	54.31	56.77

### IV. CONCLUSION

The strength and organoleptic properties of the experimental leathers are generally comparable to those of the control leathers. One of the main benefits of our work is the lower environmental impact. The spent tan liquor analysis shows significant reductions in COD, BOD<sub>5</sub> and TDS loads compared to a conventional chrome tannage. Hence, these results suggest that this semi alum tanning system can be used commercially for making garment leather.

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