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Green Technology for Leather Manufacturing: Combined Organic Tanning Based on Garad and Glutaraldehyde

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***Abstract*—The leather tanning in the modern leather industry is dominated by chromium salts, because it gives leather unmatchable hydrothermal stability and excellent organoleptic properties. However, the problem of the pollution caused by chromium is being questioned. Combination tannages are thus considered as suitable alternatives for a chrome-free tanning system. In this study, organic combination tanning process based on garad powder (Acacia nilotica sub. sp. nilotica) and glutaraldehyde syntan for the production of upper leathers is presented. Two tanning methods, garad followed by glutaraldehyde (garad-glutaraldehyde) and glutaraldehyde followed by garad (glutaraldehyde-garad), have been tried. The combination tannage, employing 20% garad powder and 3% glutaraldehyde syntan results in leathers with shrinkage temperatures of 101°C. The change in the order of addition of garad and glutaraldehyde showed a marginal difference in thermal stability, but significant variations were observed in the physical characteristics of leathers. The combination tanning system provides a significant reduction in the discharge of total dissolved solids in the wastewater. The characteristics of the leathers indicate that the garad-glutaraldehyde combination tanning system provided leathers with good organoleptic properties and comparable strength properties. The leathers were further characterized by chemical analysis. The work presented in this paper establishes the use of garad and glutaraldehyde as a potential viable alternative cleaner tanning method for tanners.**

***Keywords*— Garad; glutaraldehyde; Combination tanning; Cleaner tanning; Shrinkage temperature**

INTRODUCTION

A suitable tannage as an alternative to chrome tanning should possess the following characteristics: imparting high hydrothermal stability, producing white or pale colored and lightfast leather and having low environmental impact [1]. The tanning process is based on the conversion of putrescible skin or hides to a non-putrescible material. Leather making involves operations like soaking (rehydration), liming, deliming & bating, pickling, tanning, posttanning and finishing processes [2]. Chrome tanning system in the leather industry because of the excellent qualities of chrome-tanned leather like high hydrothermal stability, good dyeing characteristics as well as softness [3]. There is an average estimation that approximately 90% of the raw hides in the world are tanned by chrome [4]. However, chrome tanning is controversial due to high Cr(III) content in the wastewater [5]. Only 60%-70% of the chrome added is absorbed by leather in the conventional chrome tanning process, and the rest is discharged into spent tan liquor (about 2-4 $g.L^{-1}$), resulting in serious environment pollution and a great waste of chrome resource [6]. Furthermore, the ecological status of chrome is now being questioned for the possible conversion from Cr(III) to carcinogenic Cr(VI) under an oxidizing environment [7]. Therefore, tanners have been showing great interest in developing chrome-free tanning technologies in recent years. But, in general, the comprehensive performance of chrome-free leather is not comparable with the chrome-tanned one [8-10].

Nowadays, there are some chromium-free mineral tanning agents, such as zirconium (IV), [11] aluminium (III) [12], titanium (IV) [13], zinc(II), [14] and iron(III) [15, 16]. These alternatives have not been able to replace chromium for various reasons. Aluminium (III) is only a pseudo transition metal ion which forms outer orbital complexes with poor stability resulting in reversible tanning. So conventional aluminum tanning is characterized by its poor wash fastness. Zirconium (IV) and titanium (IV) are d^0 metal ions, whose crystal field stabilization energies are zero and hence, also produce reversible tanning. Zr (IV) is also acidic and has the tendency to polymerize extensively even at low pH conditions resulting in coarse-grained leather [17]. Iron tanning is considered as an alternative due to close similarities between the aqueous chemistry of chromium (III) and iron (III), but the iron (III)-tanned leathers are hard to store. During the past few decades combination tannages have been developed to avoid the use of chrome, such as tannages of vegetable tannins with aldehyde compounds or with metal tanning agents [18-20]. Among these tannages, the combination of vegetable tannins and Al is a promising option that produces leathers with high hydrothermal stability comparable to that of chrome-tanned leather [21]. Vegetable tanning has been considered as a suitable ecofriendly option to replace chromium. However, vegetable tanning has some shortcomings such as the fullness of veg leathers which prevents its use for some end products. Vegetable tannins are also difficult to biodegrade [22]. Pure vegetable tannages are not suitable as chrome replacements, while combination tannages employing vegetable tannins and metal salts or aldehyde compounds are potential alternatives to chrome tanning, capable of producing hydrothermally stable leathers [23].

Glutaraldehyde in the form of syntan has been used ina wide variety of situation to improve the quality of leather. It increases the perspiration resistance andsoftness of the leather and improves its response to dyeing. At present three forms of glutaraldehyde are commercially used for leather making viz., glutaraldehyde (unmodified), glutaraldehyde modified with alcohols and glutaraldehyde modified with alcohols and polymer (eg. ReluganTM GTW). All of the modified versions of glutaraldehyde in the market are an attempt to solve two very different problems associated with the use of glutaraldehyde alone; the unpleasant odor and the rapid reactivity of the glutaraldehyde, which causes it to react superficially with collagen matrix thereby hindering further penetration [24].

Vegetable tanning agents, of which the main components are plant polyphenols, which are of variable size are held to the collagen by Van der Waals forces and phenolic hydroxyl groups, aliphatic hydroxyl groups, phenolic carboxyl groups combined with the -OH, $-NH_2$, -COOH, -NH-CO- on the side chain of the collagen via hydrogen bonds which improves the tensile strength and tear strength of leather [25]. There are two types of vegetable tannins: condensed tannins (Fig. 1) and hydrolysable tannins (Fig. 2).

Sudan has various indigenous tanning materials. Some of these, such as Garad pods (*Acacia nilotica subsp. 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 [26].

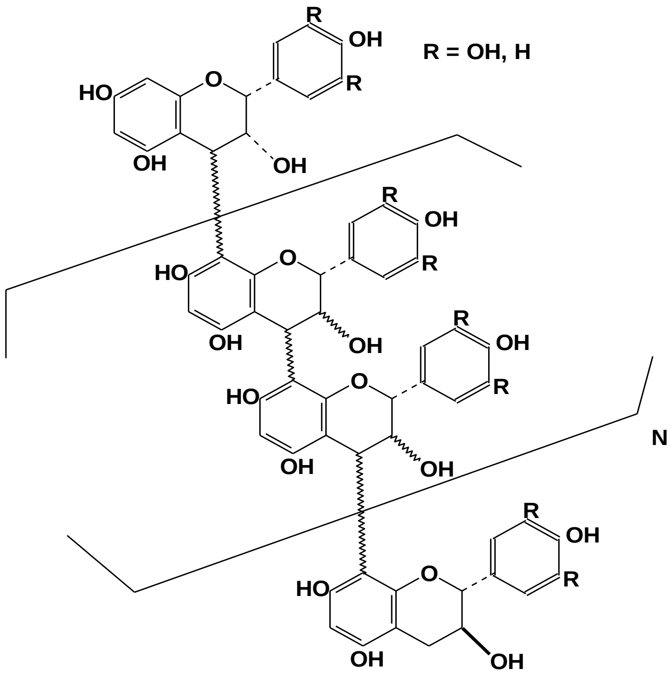

***Figure 1**: Condensed Tannin*

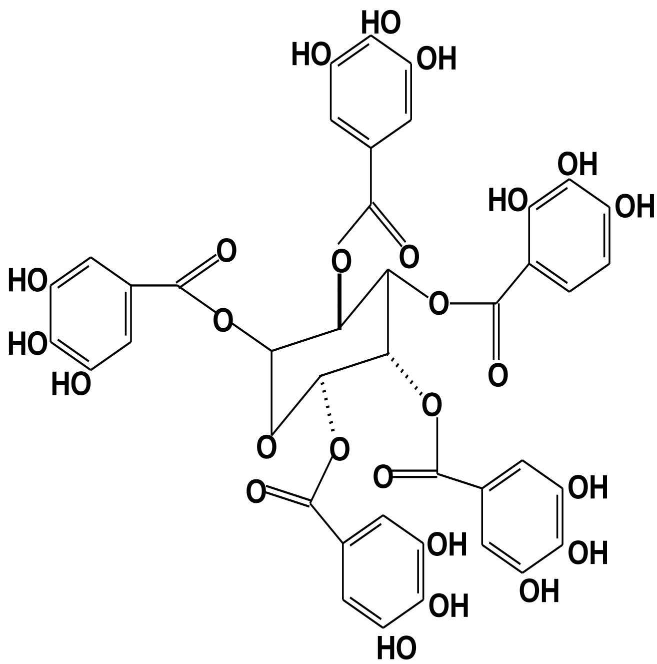

Figure 2: Hydrolyzable tannin

When garad pods are crushed, they disintegrate into three parts, the husk with about 12% pure tannins, the seeds with no tannin content and the grain powder with approximately 55% tannins. The seeds and husk form about 63.6% of the weight of the pod, the remainder being the grain powder [26]. Recently, rural garad tanned crust leathers improved for production of semi-alum shoe upper leathers [27] and also a combination tanning process based on garad powder (*Acacia nilotica sub. sp. nilotica*) and tetrakis hydroxymethyl phosphonium sulphate (THPS) for the production of upper leathers is presented as a cleaner alternative [28]. Owing to the abundant availability of garad and the presence of mixture of several polyphenolic compounds with varied molecular weight, an attempt has been made in this study to utilize them in combination tannage with Glutaraldehyde syntan (Relugan GTW).

MATERIALS AND METHODS

Materials

Conventionally processed pickled goat skins were used for tanning studies. Garad pods were sourced from Sudan. Glutaraldehyde syntan (Relugan GTW) was procured from BASF India Ltd. Chemicals used for post tanning were of commercial grade. Chemicals used for the analysis of spent liquor were analytical grade reagents.

Garad–Glutaraldehyde Combination Tanning

The tanning experiments were carried out using pickled goatskins. Experimental tanning trials employing glutaraldehyde syntan followed by garad powder (Glu-Garad) were carried out as per the process mentioned in Table I and combination tanning based on garad followed by glutaraldehyde (Garad-Glu) was carried out as per the process mentioned in Table II. Control Garad tanning trial was carried out as per process given in Table III**.** The post tanning process mentioned in Table IV is followed for both experimental and control leathers.

Determination of Shrinkage Temperature

Shrinkage temperature (referred to as Ts) is one of the most important parameters in characterizing the thermal stability of leather. It is the temperature at which the leather sample starts to shrink in water or other heating medium. Rapid and accurate determination of Ts is of great significance for the industrial leather production process as well as professionals' in-depth research [29]. The shrinkage temperature of both control and experimental leathers were determined using the Theis shrinkage tester [30]. A 2cm sample, cut out from the leather was clamped between the jaws of the clamp, which in turn was immersed in a solution of glycerol: water mixture (3:1). The solution was stirred using mechanical stirrer attached with the shrinkage tester. The temperature of the solution was gradually increased and the temperature at which the sample shrinks was noted. Triplicates were carried out for each sample and the average values are reported.

Table I. Formulation of Glu-Garad Combination Tanning Process for Goat Pickled Skin

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	50 0.75	Water Sodium bicarbonate	3×15	pH 4.5-4.7
Tanning	3	Glutaraldehyde syntan (Relugan GTW)	90	
	2	Basyntan P (phenolic syntan)	30	
	10	Garad powder	120	
	10	Garad powder	120	
Fixing	1.0	Formic acid	3× 10 + 30	pH 3.5
Washing	300	water	10	Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

Analysis of Exhaustion of Tanning Spent Liquors

Spent garad liquor from control and experimental tanning processing was collected and analyzed for the concentration using a spectrophotometric method by measuring the absorbance value at the λmax of the garad used, after suitably diluting the spent liquor using UV–visible spectrophotometer (Hitachi, Japan).

$$\% \text{ Garad exhaustion} = [(Co - Cs)/Co] \times 100$$

Where Co is the concentration of garad offered and Cs is the concentration of garad in the spent liquor. Each value reported is an average of four measurements.

Table II. Formulation of Garad-Glu Combination Tanning Process for Goat Pickled Skin

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	100 0.75	Water Sodium bicarbonate	3× 15	pH 4.5 -4.7
Tanning	2	Basyntan P (phenolic syntan)	30	
	10	Garad powder	120	
	10	Garad powder	120	
	3	Glutaraldehyde syntan (Relugan GTW BASF)	90	
Fixing	1	Formic acid	3×10+30	pH 3.5
Washing	300	Water	10	Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

Analysis of Spent Liquors from Tanning Trials

The spent tannin liquor from control and experimental tanning processes was collected, filtered and analyzed for chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), and total dissolved solids (TDS) as per standard procedures [31].

Table III. Formulation of Garad Tanning Process for Goat Pickled Skin

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	100 0.75	Water Sodium bicarbonate	3× 15	pH 4.5-4.7
Tanning	2	Basyntan P (phenolic syntan)	30	
	10	Garad powder	120	
	10	Garad powder	120	
Fixing	0.25	Formic acid	3× 10 + 30	pH 3.5
Washing	300	Water	10	Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

Visual Assessment and Hand Evaluation of the Crust Leather

Experimental and control crust leathers were 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 points indicate better property.

Physical Testing of Leathers

Samples for various physical tests from experimental and control crust leathers were obtained as per IULTCS methods [32]. Specimens were conditioned at 20±2°C and 65±2% R.H over a period of 48 hrs. Physical properties such as tensile strength, percentage elongation at break, [33] grain crack strength [34] and tear strength [35] were measured as per standard procedures. Each value reported is an average of four samples (2 along the backbone, 2 across the back bone).

Table IV. Formulation of Post-tanning Process for Experimental and Control

Process	%	Product	Duration (min)	Remarks
Washing	200	water	10	
Neutralization	0.75	Sodium bicarbonate	3× 15	pH 4.8-5.0
Retanning, Dyeing and fatliquoring	100	water		
	2	Relugan RE (Acrylic syntan)	40	
	2	Lipoderm liquor SAF (Synthetic fatliquor)	40	
	2	Basyntan DI	30	
	3	Acid dye brown	30	
	3	Lipoderm liquor SAF (Synthetic fatliquor)		
	4	Balmol BL II	40	
	3	Basyntan DI		
	4	Basyntan FB6 (phenolic syntan)	40	
Fixing	1	Formic acid	3× 10 + 30	pH 3.5
Washing	300	water	10	Drain the bath and pile overnight. Next day sammed and set, hook to dry, toggled, trimmed and buffed.

Chemical Analysis of Leathers

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 [35]. Triplicates were carried out for each sample and the average values are reported.

RESUTLS AND DISCUSSION

Combination tannages are considered suitable alternatives for chrome-free tanning systems and higher hydrothermal stability can be achieved through the use of organic combination tannages. Combination tanning trials using garad and glutaraldehyde syntan were carried out with 3% offer of glutaraldehyde syntan and 20% offer of garad. The shrinkage temperature data of leathers tanned with Garad-Glu and Glu-Garad combination along with garad control is given in Table V. From the table it is seen that both the combinations resulted in leathers with better shrinkage temperature than control leathers (garad tanned). The shrinkage temperature of leathers obtained from Garad-Glu combination tanning is higher than Glu-Garad. However the combination tanning resulted in leathers with shrinkage temperature of 101^{o}C, which is much better than control garad leather of Ts 84^{o}C.

Table V. Shrinkage Temperature of Crust Leathers for Experimental and Control

Experiment	Shrinkage temperature, Ts (^{o}C)
Glu-Garad	92±2
Garad-Glu	101±1
Garad (Control)	84±0.5

Environmental Tolerability-Spent Liquor Analysis

The spent tan liquor in both control and experimental process contains high organic matter which could lead to the contribution of high COD, dissolved and suspended solids. Hence, it is vital to assess the environmental impact from control and experimental tanning processes. The COD, BOD_5, and TDS of the spent liquor for experimental and control trials have been determined and are given in Table VI. From the table, it is observed that the COD, BOD_5 and TDS of the spent liquor processed using both the experimental tanning systems are lower than that for the spent liquor from Garad tanning (control). The BOD_5 and TDS of the spent liquor processed from Garad and glutaraldehyde combination tanning trials have significantly reduced values compared to the spent liquor of Garad control tanning trial. This could be due to increased exhaustion of Garad during tanning which is also observed from the exhaustion data of Garad given in Table VII.

Table VI. Characteristics of spent tan liquor from experimental and control processing

Experiment	COD (mg/l)	% reduction in COD	BOD_5 (mg/l)	% reduction in BOD	TDS (mg/l)	% reduction in TDS
Garad (control)	118200±2850	-	25200±950	-	92200±1550	-
Glu-Garad	102800±3450	13	15600±1150	38	74650±1050	19
Garad-Glu	94500±1450	20	1310±800	48	60850±1600	34

Analysis of Garad Exhaustion

The exhaustion of garad for both experimental and control (garad tanning) trials were determined and are given in Table VII. From the Table it is seen that the uptake of garad is better for experimental (Glu-Garad tanning and Garad-Glu tanning) compared to control leathers (Garad tanning). The exhaustion of the Glu-Garad tanning is 87% compare to Garad-Glu tanning, of 86% whereas for the control the exhaustion is about 76%.

Table VII. Exhaustion % for Garad used for Crust Leather of Experimental and Control

Experiment	Exhaustion %
Glu-Garad	87±2
Garad-Glu	86±3
Garad (control)	76±2

Bulk Properties of Leathers-Hand Evaluation of Leathers

The organoleptic properties (visual assessment) of crust leathers for experimental and control is given in Fig.3. From the figure, it is observed that Garad-Glu tanning experimental crust leathers exhibited good softness, fullness, smoothness, general appearance and dye uniformity compared to control leathers from Garad tannage. The organoleptic properties of the Garad-Glu crust leathers are better compared to Glu-Garad crust leathers.

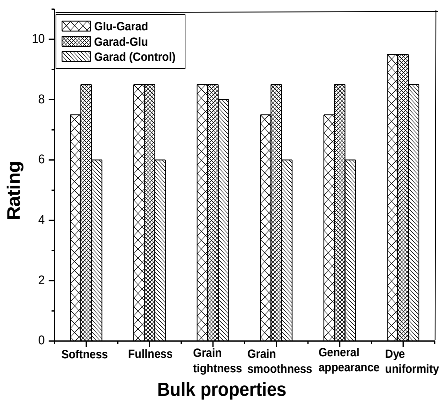

Figure 3: Graphical representation of organoleptic properties of the Experimental and control leather

Strength Characteristics of Experimental and Control Crust Leathers

The physical strength measurements of matched pair experimental (Glu-Garad and Garad-Glu) and control leathers (garad) are given in Table VIII. The physical strength measurements viz., tensile strength, elongation, tear strength, load at grain crack and distension at grain has been found to be comparable. The experimental tanning resulted in leathers with good physical strength characteristics compared to control leathers.

Chemical Analysis of the crust leather

The chemical measurements of matched pair experimental crust leather (Glu-Garad, Garad-Glu) and control (garad) are given in Table IX. 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 with glutaraldehyde combination.

Table VIII. Physical Strength Characteristics of Crust Leather of Experimental and Control

Parameter	Glu-Garad	Garad-Glu	Garad (control)
Tensile strength (Kg/cm^2)	228±2	251±2	205±2
Elongation at break (%)	54±0.62	48±0.54	41±1.58
Tear strength (Kg/cm)	54±0. 67	65±0. 67	40±0.71
Load at grain crack (kg)	40±0.69	36±0.45	25±0.69
Distention at grain crack (mm)	11±0.64	12±0.64	10±0.61

Table IX. Chemical Analysis of crust leather of experimental and control

Parameter	Garad (control)	Glu-Garad	Garad-Glu
Moisture %	13.30	14.20	13.40
Total ash content %	2.70	2.20	2.30
Fats and oils %	3.60	3.10	3.30
Water soluble matter %	5.10	3.50	3.60
Hide substance %	52	51	50
Insoluble ash %	1.20	1.50	1.40
Degree of tannage %	47.70	52.35	56.60

CONCLUSION

An organic tanning system as a substitute for chrome tanning is considered as a suitable alternative owing to the limitations of inorganic tanning agents. Though chromium is considered as the best mineral-tanning agent to date it has its own negative image as well. In the present study, an attempt has been made to produce upper leather using combination tanning process based on garad and glutaraldehyde tannage. It is seen that Garad-Glu combination tanning system with 20% garad and 3% glutaraldehyde syntan produced leathers with shrinkage temperature of 101^{o}C, which is 17^{o}C more than control leathers. The exhaustion of garad for the combination system is 10% more than the garad treated leathers. The physical and chemical analysis indicates that the experimental leathers are comparable to control leathers in terms of all the properties. The bulk properties for the experimental leathers are better than control leathers. It is possible to manufacture lighter shade upper leathers from Garad -Glu combination with a shrinkage temperature of 101^{o}C.

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