An Eco-benign Organic Combination Tanning System for Manufacture of Garment Leathers

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Abstract— Tanners have been showing great interest in developing chrome-free tanning technologies in recent years and nowadays, the chrome-free leather is more favoured in the market. Oxazolidine is a tanning agent with a high affinity to the natural proteins. Mainly it used in combination with tanning material either vegetable or synthetic, gives more softness, fullness and lightweight leather compared to standard leather. Combination tanning using vegetable tannins and oxazolidine has been proved to be a preferred alternative to chrome tanning. In this study, organic combination tanning process based on garad powder (*Acacia nilotica sub. sp. nilotica*) and oxazolidine for the production of garment leathers is presented. Garad pods powder extract has been utilized in the combination tanning system with oxazolidine. Garad tanned leathers from sheep skins used as control leathers. It has been observed that garad - oxazolidine combination tanning which employs 20% garad pods powder extract and 5% oxazolidine provides a shrinkage temperature of 103°C, which is 19°C more than the control leathers. The characteristics of the leathers indicate that the garad -oxazolidine combination system provides leathers with good organoleptic properties and comparable strength properties. The experimental tanning system provides significant reduction in the discharge of total dissolved solids in the wastewater. The leathers have been further characterized for chemical analysis. The leathers obtained from the combination system are lighter in color compared to control leathers. The manufacture of garment leathers using combination of garad and oxazolidine suggest that this tannage is a promising alternative to traditional chrome tanning.

Keywords— Garad; Oxazolidine; Combination tanning; Garment leather; Chrome free

INTRODUCTION

Tanning is a multi-steps process whereby a perishable animal hide or skin is converted into leather, which resists microbial attack and may last indefinitely. Biologically, the skin is connective tissue, comprised mainly of the extracellular matrix, a fibrous collagen structure. Tanning stabilizes the collagen matrix, protecting it against heat, water, and microbes [1].

Chrome tanning has been used for more than 100 years and about 90% of all the tanneries in the world have adopted chrome tanning [2]. Though chromium is considered as the best mineral tanning agent which leads to high hydrothermal stability, i.e. shrinkage temperature (Ts) over 100°C [2], it has a negative image. During tanning, the chromium may not be fully absorbed, and 20%-30% of chromium is discharged in the waste liquor so that it is wasted and the environment is polluted. In recent years, researchers have found that the Cr (III) is easy to oxidize to Cr(VI) by light, heat, sweat, chemical materials, etc and that it is a proven carcinogen [3-5]. So there is a requirement for an eco-friendly tanning process. Chrome-free tannage is an eco-friendly tannage. Nowadays, chrome-free leather is more and more favoured in the market and so it makes sense to study chrome -free tannages. Moreover, other tanning agents such as vegetable tannins, oxazolidine, aluminium, titanium, zirconium have associated disadvantages [6-8]. Combination tannages are thus considered as suitable alternatives for a chrome-free tanning system. Amongst the innumerable combination tannages that are currently exploited, vegetable tannins and oxazolidine combination tannages; vegetable tannins and aluminium tanning agent combination tannages are the most promising options. They have different mechanisms in improving the stability of collagen. In the process, oxazolidine

and aluminium act as crosslinkers so that it is possible to achieve a hydrothermal stability comparable that of chrome-tanned leather [9-11].
Oxazolidines, heterocyclic derivatives, are synthesized using amino-hydroxy compounds and aldehydes as raw materials [12]. In the 1970s, oxazolidines were developed and patented as a new class of tanning agent [7]. Among the oxazolidines, oxazolidine A and oxazolidine E (Fig. 1 and Fig. 2) have been produced and studied extensively for their use as tanning agents [13]. Oxazolidine will react with the amino groups of collagen to form cross-links to improve the shrinkage temperature of leather [7,14]. Under hydrolytic conditions, the rings open to form an N-hydroxymethyl compound, which can react with one or more amino groups to produce effective cross-linking (Fig. 3) [5].

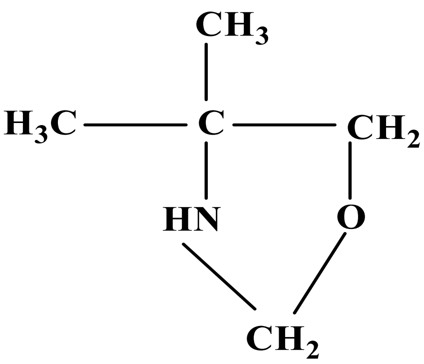

***Figure 1**: Oxazolidine A*

BIOTAN G100 (Heterocyclic synthetic tanning agent) is a concentrated oxazolidine product with excellent tanning properties. When used alone BIOTAN G100 produce leather with a good mellow full hand, fine grain, good tear resistance and of a light yellow colour. The more common use of BIOTAN G100 is in the pretanning of vegetable and chrome leather as well as retanning agent to improve mellowness, tear resistance and grain appearance. BIOTAN G100 used in pretanning of chrome leather improve fullness, softness of final article and the exhaustion of the tanning float. BIOTAN G100 is fully functioning in a range of pH from 3,5 to 9, therefore can be used without any adversity during retanning before or after neutralization[15].

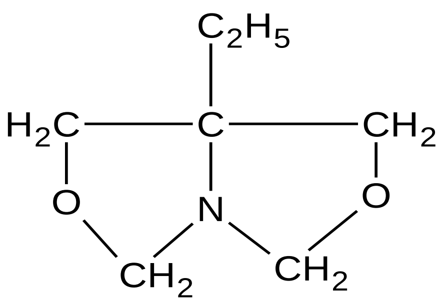

Figure 2: Oxazolidine E

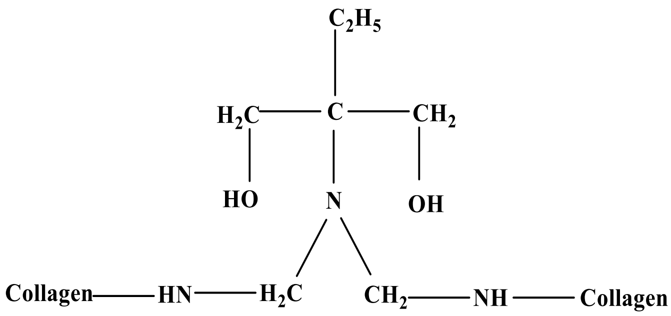

Figure 3: Ring opening of oxazolidine and cross-linking of collagen with oxazolidine.

Bio-active ingredients in the form of tannins are present in some of the plant materials capable of imparting tanning effect. Vegetable tanning is one of the traditional and eco-friendly processes in leather making involving plant materials [16]. The vegetable tannins are water-soluble polyphenolic compounds having molecular weight in the range of 500 –3000 Daltons [17, 18]. Based on their chemical structure, the vegetable tannins are classified as Hydrolysable type (e.g. Myrobalan) and Condensed type (e.g. Wattle).
To the rural tanner of tropical and subtropical Africa and Asia, the acacias are one of the most important tannin-bearing trees. Several species, suc h as *Acacia Arabica*, *A. nilotica* and *A.adamsonia*, have supplied pods and bark since immemorial times.The leather produced by acacia pods is soft, plump, light colored and durable, and it can be readily dyed. The acacia pods and bark are known variously in the countries where they grow as babul (hindustan), babar (Sind) garad or sunt (Sudan), neb neb (*West Africa*) and gabarua (Nigeria) [19]. The pods used for tanning are from 10 to 15 centrimeters long and 1 centimeter broad, and they have 8 to 10 seeds. Contrary to common belief, the seeds do not contain tannin, which is present only in the pods. According to the conditions of the soil and the climate, their tannin-content varies from 20 to 30%. The material contains an undue proportion of nontans and a high proportion of sugary matter in the seeds. This results in a rapid fermentation of the liquor [19].
The bark of the *Acacia Arabica* does not contain more than 14% tannin and is mostly used in northern India under the name of babul bark. The bark from old trees yields a very dark colored tannin. It is best, therefore, to strip from trees which are from five to seven years old. When babul bark is used for tanning, it gives a leather which has a darker color and a tendency to crack and tear; but when it is suitably blended with myrobalan (3:1) or with a varam bark, it can be used with advantage, particularly in sole leather tannage [19]. *Acacia nilotica* (Sunt in Arabic) is a member family of subfamily *Mimosoidae* of leguminous trees. It is of multiple uses in the Sudan, Africa and many Arabic countries. The tree is readily distinguished by

the long white spines, yellow head inflorescene and the grey necklace-like pods. Three subspecies are commonly found in the Sudan, namely *tomentosa* that characterized by the pubescent pods and grow throughout Sudan, *nilotica* that characterized by the glabrous pods and grow along the White Nile and *adansonii* that characterized by the broad pods and grow in western Sudan [20].The pods of ssp. nilotica have been used for tanning in Egypt for over 6 000 years. The inner bark contains 18-23% tannin, which is used for tanning and dyeing leather black. Young pods produce a very pale tint in leather, notably goat skins. Extracts from the bark, leaves and pods are used for dyeing cotton, silk and leather [19].

Since the garad extract contains natural products of relatively high molecular weight which have the ability to complex strongly with collagen, an attempt has been made in this study to utilize them in combination tannage with Oxazolidine.

MATERIALS AND METHODS

Materials

Conventionally processed pickled sheep skins were taken for the combination tanning trials. Garad pods were sourced from Sudan and BIOTAN G100 (Oxazolidine) procured from Biokimica Group-Italy. Chemicals used for post tanning were of commercial grade. Chemicals used for the analysis of spent liquor were of analytical reagent.

Preparation of Aqueous Extraction of Tannins from Garad Pods

Dry garad pods obtained from Sudan were grounded into powder. Ground garad pods of known quantity have been soaked in water (1:10 w/v) at a temperature of 80±2^{o}C in water bath for one hour, filtered through a piece of cotton cloth and concentrated and used in combination tanning. The total soluble content of the garad pods extract was determined to be 56±1%.

Tanning Trials

The tanning experiments were carried out on pickled sheep skins. Experimental combination tanning trial oxazolidine followed by garad (Oxaz-garad) were carried out as per the process mentioned in Table I and combination tanning based on garad followed by oxazolidine (Garad -Oxaz) 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. Both experimental and control leathers were processed into garment crusts following the post – tanning process mentioned in Table IV.

Determination of Shrinkage Temperature

The shrinkage temperature of both control and experimental leathers were determined using the Theis shrinkage tester [21]. A 2 cm 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.

Visual Assessment 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

Samples for various physical tests from experimental and control crust leathers were obtained as per IULTCS methods [22]. Specimens were conditioned at $20 \pm 2\,^{o}$C and 65 ± 2 % R.H over a period of 48 hrs. Physical properties such as tensile strength, percentage elongation at break, [23] grain crack strength [24] and tear strength [25] were measured as per standard procedures. Each value reported is an average of four (2 along the backbone, 2 across the back bone) samples.

Analysis of Spent Liquor

The spent liquor from control and experimental tanning processing were collected, filtered and analyzed for chemical oxygen demand (COD), Biochemical oxygen demand (BOD_5), and total Dissolve solids (TDS) as per standard procedures [26].

Table I. Formulation of Oxaz-Garad Combination tanning process for Sheep pickled skin

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	50	Water		
	1	sodium bicarbonate	3× 15	pH 6
Tanning	5	Oxazolidine-Biotan G100 (Biokimica)	90	
Garad tanning	2	Phenolic syntan	30	
	10	Garad extract	120	
	10	Garad extract	120	
Fixing	0.5	Formic acid	3× 10 + 30	Check the pH to be 3.5. Drain the bath and pile overnight. Next day sammed and shaved to 0.8 mm. The shaved weight noted.
Washing	300	Water	10	

Chemical Analysis of Leathers

The chemical analysis was carried out for control and experimental leathers according to the standard procedures [27], for total ash content, % moisture, % oils and fats, % water soluble, % hide substance, % insoluble ash and degree of tannage. Triplicates were carried out for each sample and the average values are reported.

RESUTLS AND DISCUSSION

Combination tanning trials using garad extract and oxazolidine (Biotan G100) were carried out with 5% offer of oxazolidine and 20% offer of garad powder. The shrinkage temperature data of leathers tanned with Garad - Oxaz and Oxaz- Garad combination along with garad control is given in Table V**.** From the table it is seen that both the combination resulted in leathers with good shrinkage temperature. The shrinkage temperature of leathers obtained from Garad -Oxaz combination tanning is slightly higher than Oxaz- Garad. However, both the combination tanning resulted in leathers with shrinkage temperature greater than 97^{o}C, which are better than control leathers from Garad of Ts 84^{o}C.

Table II. Formulation of Garad-Oxaz Combination Tanning Process for Sheep Pickled Skin

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	100	Water		
	0.75	Sodium bicarbonate	3× 15	pH 4.5 -4.7
Tanning	2	Phenolic syntan	30	
	10	Garad extract	120	
	10	Garad extract	120	
	5	Oxazolidine - Biotan G100 (Biokimica)	90	
Fixing	0.25	Formic acid	3× 15	pH 4
Washing	300	Water	10	Check the pH to be 3.5. Drain the bath and pile overnight. Next day sammed and shaved to 0.8 mm. The shaved weight noted.

Ecological Impact - Spent Liquor Analysis

The spent tan liquor contains highly organic matter in both control and experimental process liquor and it contributes to extremely high COD, dissolved and suspended solids. Hence, it is vital to assess the environmental impact from control and experimental tanning process. 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 system are lower than the spent liquor from Garad tanning (control). The BOD_5 and TDS of the spent liquor processed from Garad and Oxaz combination tanning trials have significantly reduced compared to the spent liquor of control Garad tanning trial.

Table III. Formulation of Garad Tanning Process (Control) for Sheep Pickled Skin

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	100	Water		
	0.75	Sodium bicarbonate	3× 15	pH 4.5 -4.7
Tanning	2	Phenolic syntan	30	
	10	Garad extract	120	
	10	Garad extract	120	
Fixing	0.25	Formic acid	3× 10 + 30	pH 3.5 Check the pH to be 3.5. Drain the bath and pile overnight. Next day sammed and shaved to 0.8 mm. The shaved weight noted
Washing	300	Water	10	

Tactile Properties of Crust Leathers for Experimental and Control

The organoleptic properties (visual assessment) of garment crust leathers for experimental and control are given in Fig. 4**. (**Higher numbers indicate superior properties). From the figure, it is observed that crust leathers processed by experimental combination tanning system exhibited good softness, fullness, smoothness, general appearance and dye uniformity compared to control leathers from Garad tannage. The organoleptic properties of the Garad - Oxaz crust leathers are slightly better compared to Oxaz- Garad crust leathers.

Table IV. Formulation of Post-tanning Process for Making Garment Crusts

Process	%	Product	Duration (min)	Remarks
Washing	200	Water	10	
Neutralization	0.75	Sodium bicarbonate	3× 15	pH 5-5.5
Retanning	100	Water		
	8	Syntan	90	
Fatliquoring	9	Synthetic fatliquor	40	
Dyeing	3	Acid dye brown	30	
Fixing	1	Formic acid	3× 10 + 30	pH 3.5

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

Experiment	Shrinkage temperature, Ts (°C)
Oxaz- Garad	97±1
Garad -Oxaz	103±2
Garad (Control)	84±0.5

Table VI. Characteristics of Spent Liquor for Experimental and Control

Experiment	COD (mg\l)	BOD_5 (mg\l)	TDS (mg\l)
Garad (control)	124200±2550	26500±1100	102140±2000
Oxaz- Garad	109800±2000	17250±1300	50600±1250
Garad-Oxaz	108420±2650	14000±850	48450±1200

Strength Characteristics of Experimental and Control Crust Leathers

The physical strength measurements of experimental and control leathers are given in Table VII. The physical strength measurements viz., tensile strength, tear strength has been found to be better for experimental leathers. The experimental Garad - Oxaz tanning system resulted in leathers with good tensile and tear strength characteristics. The values for load at grain crack for both experimental and control leathers were comparable. All the physical strength parameters for both control and experimental leathers are found to exhibit the requirement of BIS norms. It is seen that the softness of experimental leathers are better than that of the garad control leathers.

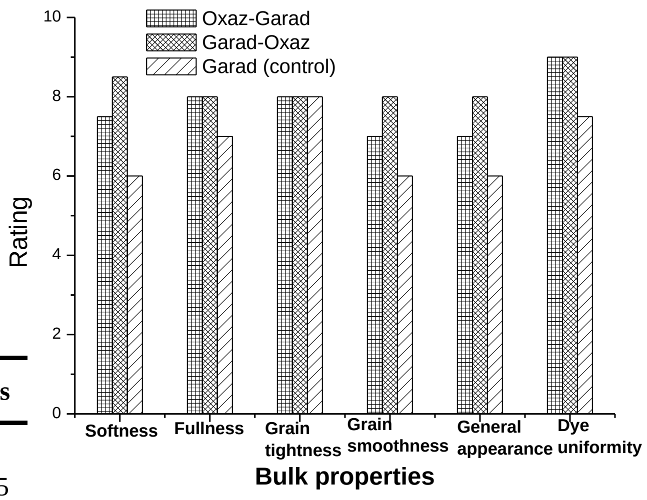

Figure 4: Graphical Representation of Organoleptic Properties of the Experimental and Control Leather

Table VII. Physical Strength Characteristics of Experimental and Control Crust Leathers

Parameter	**Oxaz-** Garad	Garad - **Oxaz**	Garad **(control)**
Tensile strength (Kg/cm^2)	186±2	198±2	174±3
Elongation at break (%)	67±2	75±4	58±2
Tear strength (Kg/cm)	53±3	66±2	49±1
Load at grain crack (kg)	24±0.7	26±0.5	21±0.5
Distention at grain crack (mm)	11±0.3	12±0.3	10±0.3

Chemical Analysis of the Crust Leather

The chemical analysis values of experimental crust leathers (Oxaz - Garad and Garad - Oxaz) and control (Garad) are given in Table VIII. The chemical analysis data for the experimental leathers is comparable to that of control leathers. However, the water soluble matter for the control leathers is more compared to the experimental leathers.

Table VIII. Chemical Analysis of Experimental and Control Crust Leathers

Parameter	Garad **(control)**	**Oxaz-** Garad	Garad - **Oxaz**
Moisture %	13.50	12.25	12.45
Total ash content %	2.65	2.20	2.60
Fats and oils %	3.45	3.30	3.15
Water soluble matter %	5.30	3.45	3.35
Hide substance %	53	52	51.50
Insoluble ash %	1.35	1.15	1.25
Degree of tannage %	44.15	53.56	54.95

CONCLUSION

Oxazolidine is a tanning agent with a high affinity to the natural proteins. Used in combination with tanning either vegetable or synthetic, gives more softness, fullness and

Light weight leather compared to standard leather. In the present study, an attempt has been made to produce garment leather using combination tanning process based on Garad and Oxazolidine. It is seen that combination tanning system with 20% Garad extract and 5% Oxazolidine results in leathers with a maximum shrinkage temperature of 103^{o}C, which is 19^{o}C greater than the control leathers. The physical and chemical analysis indicates that the experimental leathers are comparable to control leathers in terms of all the properties. The Garad -Oxaz tanned leathers are softer than control. The bulk properties for the experimental leathers are better than control leathers. One of the main benefits of this work is the lower environmental impact. The spent tan liquor analysis shows significant reductions in COD and TDS loads compared to control. It is possible to manufacture lighter shade garment leathers from garad -Oxaz combination with a shrinkage temperature of 103^{o}C.

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