International Journal of Advance Industrial Engineering
ISSN 2320 –5539

Research Article

Development of Eco-friendly Combination Tanning System for the Manufacture of Upper Leathers

A.E. Musa[*a] and G.A. Gasmelseed[a]

[a]Department of Leather Technology, College of Applied and Industrial Sciences, University of Bahri, Khartoum – Sudan, P.O.Box 12327

Accepted 26 Feb. 2013, Available online 1March 2013, **Vol.1, No.1 (March 2013)**

Abstract

More than 90% of global leather production is through chrome-tanning process currently. The conventional methods employed for tanning lead to significant material loss and serious environmental concern. The chromium salt tanning system, which is still the most popular leather tanning procedure, is under continuous pressure from environmental groups and international regulations due to pollution and toxicology reasons unfairly associating the chromium (III) commonly used with hazardous chromium (VI). Among alternative tannages that are currently exploited, the vegetable tannins and oxazolidine combination tannage is one of the most promising options. In this study, combination tanning process based on garad–oxazolidine tannage for the production of upper leathers is presented. Garad powder (Acacia nilotica spp nilotica pods) has been utilized in the combination tanning system with oxazolidine. It has been observed that garad-oxazolidine combination tanning employing 20% garad powder and 4% oxazolidine provides a shrinkage temperature of 102oC. The characteristics of the leathers indicate that the garad-oxazolidine combination system provides leathers with good organoleptic properties and comparable strength properties. The leathers have been further characterized for chemical analysis. The manufacture of upper leathers using combination of garad and oxazolidine appears to be promising.

Keywords: *Oxazolidine, Garad powder, Acacia nilotica spp nilotica pods, Upper leather, Combination tanning*

1. Introduction

Leather processing involves a series of operations. The operations involved in leather processing may be classified in three groups: pretanning or beamhouse operations, tanning, and post tanning as described by Ramasami and Prasad (1991). Pretanning operations aim at cleaning hides/skins, tanning stabilizes the skin/hide matrix permanently, and aesthetic values are added during post tanning and finishing operations.

During the last twenty years new tanning methods, which allow avoidance of toxic chromium compounds, have been developed. Although such tanning methods enable the avoidance of chromium compounds, it does not mean that the leather is free from inorganic salts (aluminum, silicon, titanium etc.). Due to increasingly strict requirements for leather and with regard to recycling of leather wastes, the manufacture of chromium-free leather becomes very important (Plavan et al., 2009).

Developing of environmentally friendly tanning technologies, most perspective is the combination of inorganic (aluminium, silica, zinc etc.) and organic (vegetable tannins, resins,aldehydes etc) chrome-free materials (Covington & Lampard, 2004; Rosca, et al., 2008; Madhan et al., 2005; Saravanabhavan, et al., 2007). The deep interest in clean technologies and stringent norms set by regulations; have led the tanners to increase their efforts to develop chrome free tanning agents. Chromium-free leathers have advantages, like the lack of chromium in the effluents, obtaining fully recyclable shavings and end-products for agricultural applications, no risk of Cr (VI) formation, metal free leathers, improved sorting in the pre-tanned stage, and white and light colored, brilliant leathers. Therefore, different markets require the manufacture of chrome-free leather to have comparable properties to chrome tanned leather such as feel, fullness, softness, and hydrothermal stability. It has been suggested that the environmental impact of chromium could be alleviated by substituting all or part of the offer by other metal tanning salts, when the following options are the likeliest candidates: Al(III), Ti(III)/(IV), Fe(II)/(III), Zr(IV), and La(III). Other alternative tanning options can be polyphenols, oxazolidine, formaldehyde, polymers, carbohydrates, etc. (Covington, 2008).

The compounds of divalent chromium ion (Cr II) such as CrO, $Cr(OH)_2$, $CrSO_4$ and $CrCl_2$ are powerful reducing agents and mostly stable under anaerobic conditions. Trivalent state of chromium (Cr III) is the most stable oxidation state of chromium and forms a large number of

---

*Corresponding author's Email: ali206w@hotmail.com complexes, which are usually octahedral in shape. The hexavalent chromium metal ion is a powerful oxidizing agent. $K_2Cr_2O_7$ and K_2CrO_4 are the classic examples of compounds containing chromium in this oxidation state. Chromium IV and V are intermediate oxidation states but usually unstable. However, efforts have been made to stabilize these unusual oxidation states in suitable ligand environment (Ramasami et al., 1995). Chromium (III) is considered to play an important role in glucose, lipid and protein metabolism (Hayes, 1982). The physiological importance of Cr(VI) is highly toxic, mutagenic and carcinogenic to humanity and animals (Appennoth et al., 2000) causing damage to skin, mucous membrane and respiratory tract (Katz & Salem, 1994). Dermal contact with Cr(VI) compounds can cause allergic dermatitis, while this effect has not been generally observed for Cr(III) compounds (Katz & Salem, 1994). Hexavalent chromium is rapidly taken up by the cells through the sulfate transport system (Sugiyama, 1992). Hexavalent chromium in the presence of glutathione has been demonstrated to produce genotoxic DNA adducts that inhibit DNA replication (Snow, 1990). Cr(VI) readily passes through cell membranes and produces a number of potentially mutagenic DNA lesions upon intracellular reduction to Cr(III). Tolerance limit in air (as Cr_2O_3) is 0.1 mg/m^3 of air for human beings.

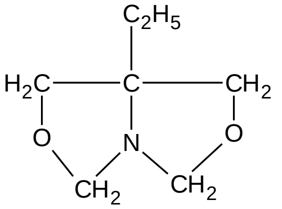

Fig. 1 1-aza-3, 7-dioxabicyclo-5 methyl (3,3,0) octane (Oxazolidine E or II)

The research centers throughout the world have undertaken studies on new tanning processes and have updated old methods in an attempt to find an alternative to conventional chrome tanning (Gratacos et al., 1993). Till date there is no effective substitution for chrome tanning system. Chrome tanned leathers possess high stability to wet heat and they have shrinkage temperature above 100°C. Considerable research has shown that the tanning effects of minerals other than chromium (Al, Zr, Ti, or Fe) are enhanced when they are used in combination with vegetable tannins, aldehydes, or other organic molecules (Sundarrajan et al., 2003; Fatima et al., 2005 and Madhan, 2007). Leather tanned with these combinations had Ts of near 100°C and physical-mechanical properties adequate for variety of application. The vegetable–oxazolidine combination tanning has been adopted to make different kinds of soft leather (Gill, 1985 and Chandrababu et al., 1995). Oxazolidine has been found to be bio-degradable (Rahman, 1995). This explicates that oxazolidine is highly potent to be a retanning agent for vegetable tanned leather.

The system is also environment friendly.

Oxazolidine, a heterocyclic derivative obtained by the reaction of aminohydroxy compounds with formaldehyde (Dasgupta, 1977), is an alternative to aldehyde tannage. 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 (Dasgupta, 1977; Zhao et al., 2007 and Gunasekaran et al., 1988). Oxazolidines have been shown to possess high reactivity and good tanning ability. Leather tanned by oxazolidine owns many characteristics: good softness and fullness, good physical/mechanical properties, sweat resistance and washability. These merits recommend oxazolidines to many researchers and series of oxazolidine tanning agents have been synthesized (Dasgupta, 1977). Oxazolidine will react with the amino groups of collagen to form cross-links improving the shrinkage temperature of leather (Dasgupta, 1977; Zhao et al., 2007 and Gunasekaran et al.,1988). Leather tanned by Oxazolidine E **(**figure 1) has similar shrinkage temperature to that of glutaraldehyde tanned leather (Gunasekaran et al., 1988), but is less fullness and less hydrophilic, because the molecular weight of monomeric oxazolidine is smaller than that of polymerized glutaraldehyde.

Catechin (figure 2) was used as a model for condensed vegetable tannins, to elucidate the reaction between the flavonoid ring system and oxazolidines in the combination tannage (figure 3) and the crosslinking reaction occurs predominantly at the C-6 and C-8 of the ring A of catechin moieties. The crosslinker reacts at the C-5 of oxazolidine, by ring opening and reacting via the N-methylol intermediate (Shi et al., 1999).

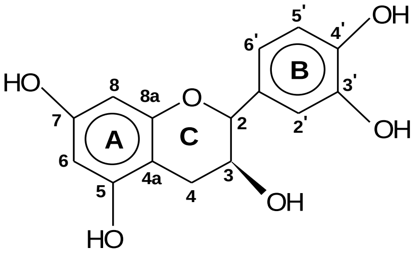

Fig. 2 Catechin

Sudan has various indigenous tanning materials. Some of these, such as Garad pods (*Acacia nilotica subsp.* <u>*nilotica*</u>) 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

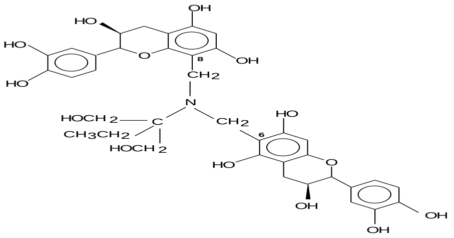

Fig. 3 Model of crosslinking catechin with Oxazolidine illustrating the major sites of reaction

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 (Gasmelseed, 1976).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 (Gasmelseed, 1976). Recently, rural garad tanned crust leathers improved for production of semi-alum shoe upper leathers (Musa & Gasmelseed, 2012). 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 oxazolidine.

2. Materials and methods

Materials

Conventionally processed pickled goat skins were taken for the combination tanning trials. Garad pods powder was sourced from Sudan. Chemicals used for post tanning were of commercial grade. Chemicals used for the analysis of spent liquor were of analytical reagent.

Garad-oxazolidine Combination Tanning

The tanning experiments were carried out using pickled goatskins. Experimental tanning trials employing oxazolidine followed by garad powder (Oxa-Garad) were carried out as per the process mentioned in **Table I** and combination tanning based on garad followed by oxazolidine (Garad-Oxa) 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** was followed for both experimental and control leathers.

Table I Formulation of Oxa-Garad Combination tanning process for goat pickled skin

Process	%	Product	Duration (min)	Remarks
Adjustment of the pH	50	Water		
	1	sodium bicarbonate	3 x15	pH 6
Tanning	4	Oxazolidine Granofin TX50(Clariant)	90	
Garad tanning	2	Basyntan P (Phenolic syntan, BASF)	30	
	10	Garad powder	120	
	10	Garad powder	120	
Fixing	0.5	Formic acid	3 x 10 + 30	pH 3.5
Washing	300	Water	10	Check the pH to be 3.5. Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

Table II Formulation of Garad-Oxa Combination tanning process for goat 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	Basyntan P (phenolic syntan)	30	
	10	Garad powder	120	
	10	Garad powder	120	
	4	Oxazolidine Granofin TX50(Clariant)	90	
Fixing	0.25	Formic acid	3× 15	pH 3.5
Washing	300	Water	10	Check the pH to be 3.5. Drain the bath and pile overnight. Next day sammed and shaved to 1.2 mm. The shaved weight noted.

Determination of shrinkage temperature

The shrinkage temperature of both control and experimental leathers were determined using the Theis shrinkage tester (McLaughlin & Theis, 1945). The thermal stability of collagen is an important property for the assessment of the quality of skin, as it indirectly indicates any structural destabilization of the skin matrix due to microbial attack. The thermal stability of stock is normally assessed by shrinkage temperature. 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 III Formulation of Garad tanning process (Control) for goat 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	Basyntan P	30	
	10	Garad powder	120	
	10	Garad powder	120	
Fixing	0.25	Formic acid	3× 10 + 30	pH 3.5
Washing	300	Water	10	Check the pH to be 3.5. 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 λ_{max} of the garad used, after suitably diluting the spent liquor using *UV–visible spectrophotometer (Hitachi, Japan).*
% Garad exhaustion = $[(C_o - C_s)/C_o] \times 100$

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

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 (Clesceri et al. 1989).

Table IV Formulation of post-tanning process for making upper crusts

Process	%	Product	Duration (min)	Remarks
Washing	200	Water	10	
Neutralization	0.75	Sodium bicarbonate	3× 15	pH 5-5.5
Pre-retannage	100	Water		
	2	Relugan RE (Acrylic syntan)	40	
Pre-fatliquor	2	Lipoderm liquor SAF (Synthetic fatliquor, BASF)	40	
	2	Basyntan DI (Phenol-naphthalene condensation syntan, BASF)	30	
Dyeing	3	Acid dye brown	30	
fatliquoring	3	Lipoderm liquor SAF (Synthetic fatliquor, BASF)		
	4	Balmol BL II (Semi synthetic fatliquor, Balmer & Lawrie)	40	
Retanning	3	Basyntan DI		
	4	Basyntan FB6 (Resin syntan based on melamine, BASF)	40	
Fixing	1	Formic acid	3× 10 + 30	pH 3.5

Table V Shrinkage temperature and garad exhaustion for experimental and control

Experiment	Shrinkage temperature, Ts (^{0}C)	Exhaustion %
Oxa- garad	98±1	88±2
Garad -Oxa	102±2	85±3
Garad (Control)	84±0.5	75±2

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 and hand evaluation of leathers

Samples for various physical tests from experimental and control crust leathers were obtained as per IULTCS methods (IUP2, 2000). Specimens were conditioned at 20 ± 2^{o}C and 65 ± 2% RH (Relative Humidity) over a period of 48 h. Physical properties such as tensile strength, percentage elongation at break (IUP6, 2000), grain crack strength [SLP9 (IUP9), 1996] and tear strength (IUP8, 2000) were measured as per standard procedures. Each value reported is an average of four samples (2 values along the backbone and 2 values across the back bone).

Chemical Analysis of leather

The chemical analysis was carried out for control and experimental leathers according to the standard procedures (Official Methods, 1965). 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.

3. Results and Discussion

Combination tanning using garad- oxazolidine with a garad offer of 4%, keeping the offer of garad constant at 20%, and changing the order of addition was carried out. Though the tanning system using garad and oxazolidine are eco-friendlier, it is essential to study the properties of the leathers whether it is comparable to that of chrome tanning system. The thermal stability of chrome tanned leathers is well known to be greater than 100^{o}C. The shrinkage temperature data for various combinations are given in Table 5. It is seen from the table that just by the use of 4% of oxazolidine in combination with garad exhibited more than 10^{o}C increase in shrinkage temperature compared to garad control leathers. The garad-oxazolidine combination tanning provides shrinkage temperature of 102^{o}C compared to 84^{o}C for control. The exhaustion of garad for oxazolidine-garad and garad – oxazolidine and control (garad tanning) are given in Table 5. It is observed that there is an increase in the amount of garad fixed in the presence of oxazolidine and increased exhaustion of garad observed can be semi-quantitatively related to the increase in shrinkage temperature of combination tanning systems of garad.

It is seen that the order of addition of garad and oxazolidine has little effect on the thermal stability of the final leathers. The control leathers exhibit a value of 84 ^{o}C. The values observed of the shrinkage temperature given in **Table V**. Oxazolidines have the potential to crosslink, as they can undergo ring opening to form a carbocationic intermediate that may interact, depending on the pH value, through covalent bonds with the amino groups of the collagen side-chains. The oxazolidines can also covalently link with the flavonoid ring system (Covington et al., 1999; Covington & Shi, 1998; D’Aquino et al., 2004). In order to achieve a high hydrothermal stability of the tanned leather, the determining mode, as reported in the literature, (Covington and Song, 1999; Lu, et al., 2003) is to simultaneously promote the formation of covalent bonds between oxazolidine and garad, thereby covalently binding a tannin matrix to collagen in a concerted interaction. The covalent binding of oxazolidine to the amino groups of collagen is favored by relatively high pH; hence the combination of garad and oxazolidine had resulted in high shrinkage temperature.

Oxazolidine bearing aldehydic group bind with side chain amino groups of lysine and arginine, whereas polyphenolic constituents of garad tend to have non-specific interaction viz., hydrogen bonding, electrostatic and hydrophobic with collagen. Hence the combination of garad and oxazolidine worked synergistically to enhance the hydrothermal stability of collagen. Variation in the order of addition of these two tanning agents resulted in changes in the bulk properties of the leathers. Tanning with oxazolidine followed by garad resulted in leathers with better fibre splitting compared to garad - oxa combination.

Oxazolidines are considered heterocyclic compounds and their bi-functional behaviour is responsible for their cross-linking reaction with phenols, epoxies, proteins and other functional group that can react with formaldehyde under alkaline conditions (Kitty et al., 2008).

Bulk properties of leathers—hand evaluation of leathers

Upper crust leathers from control and experimental processes have been evaluated for various bulk properties by hand and visual evaluation. The average rating for the leathers has been calculated for each functional property and is given in figure 4. Higher numbers indicate better property. From the figure, it is observed that oxazolidine-garad 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 oxazolidine-garad crust leathers are better compared to garad-oxazolidine crust leathers.

Physical strength characteristics of experimental and control crust leathers

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 at break, tear strength, load at grain crack and distension at grain crack were carried out for the control and experimental upper crust leathers and the data are given in **Table VI**.

Table VI Physical strength characteristics of experimental and control crust leathers

Parameter	Oxa-Garad	Garad -Oxa	Garad (control)	BIS standards
Tensile strength (Kg/cm^2)	221±2	252±2	205±30	200
Elongation at break (%)	55±0.6	58±1.5	41±1.58	40-65
Tear strength (Kg/cm)	51±1.5	60±1.5	40±0.71	30
Load at grain crack (kg)	21±0.6	25±0.6	20±0.71	20
Distention at grain crack (mm)	11±1.7	12±0.7	10±0.71	7

The strength characteristics of both experimental and control leathers are observed to be comparable. Natural tannins from plant origin are known to produce hard leathers and are generally employed for producing firm leathers. Hence, it is important to evaluate the extent of softness contributed by garad on the final leathers. The experimental leathers especially oxazolidine-garad exhibited better softness compared to the garad control leathers and garad-oxazolidine experimental leathers. The trend in the object assessment of softness values are in accordance with the observations made from visual assessment data shown in **Fig. 4**.

Chemical Analysis of the crust leather

The chemical analysis values of experimental crust leathers (Oxa-Garad and Garad-Oxa) and control (Garad) are given in **Table VII**. 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.

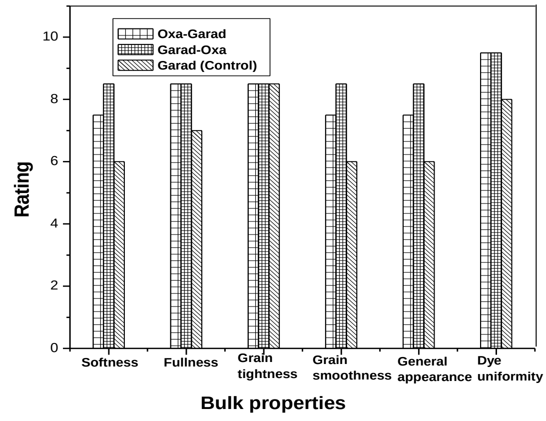

Fig. 4: Graphical representation of organoleptic properties of the experimental and control leather

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 VIII**. 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 oxazolidine 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 V**.

Table VII Chemical Analysis of experimental and control crust leathers

Parameter	Garad (control)	Oxa-Garad	Garad-Oxa
Moisture %	13.3	14.4	14.0
Total ash content %	2.7	2.0	2.1
Fats and oils %	3.6	3.4	3.2
Water soluble matter %	5.1	3.6	3.4
Hide substance %	52	51	50
Insoluble ash %	1.2	1.6	1.3
Degree of tannage %	47.7	51	56.2

Conclusion

Considerable efforts have been made to develop chrome-free tannges or to reduce the discharge of chrome in the tannery effluent. Oxazolidines, a new class of tanning agents, have demonstrated versatile uses in leather tanning and have been shown to help eliminate or reduce chrome from the tannery effluent. In the present study, an attempt has been made to produce upper leather using combination tanning process based on garad and Oxazolidine. It is seen that combination tanning system with 20% garad powder and 4% Oxazolidine results in leathers with a maximum shrinkage temperature of 102°C, which is 18°C greater than the control leathers. The exhaustion of garad is 10% more when garad is used in combination with oxazolidine compared to solo garad tanning. The physical and chemical analysis indicates that the experimental leathers are comparable to control leathers in terms of all the properties. The Garad-Oxa tanned leathers are softer than control. The bulk properties for the experimental leathers are better than control leathers. It is possible to manufacture lighter shade upper leathers from Garad-Oxa combination with a shrinkage temperature of 102°C

Table VIII 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	-
Oxa -Garad	103900±3500	12	15850±1100	37	75550±1150	18
Garad-Oxa	95700±1500	19	13350±900	47	61750±1700	33

References

Appennoth, K.J, Bischoff, M, Gabrys H, Stoeckel J, Swartz HH, Walczak T. (2000), *J Inorg. Biochem.*, 78,235.

Shi, Bi , Youle HE, Hoajun Fan, Shaoyu Zeng, Covington, A.D and Attenburrow, G.E. (1999). High stability organic tanning using plant polyphenols. Parts 2. The mechanism of the vegetable tannin-oxazolidine tannage. *J Soc Leather Technol. Chem*, 83, 8-13.

Chandrababu, N.K.; Rathnasamy, V.; Samvelu, N.; and Parthasarathy, K. (1995). Ecofiendly tanning for the production of garment leather. 39th *LERIG* , 32,.

Covington, A.D. (2008), Alternative Tanning Options. *Leather Magazine*, July, 16-22.

Covington, A. D., Lampard, G. S. (2004), Studies on Semi-metal Tanning, *J. Am. Leather Chemists Assoc.*, 99, 502-509.

Covington, A.D. and Shi, B. (1998). High stability organic tanning using plant polyphenols. Part 1: The interactions between vegetable tannins and aldehydic crosslinkers, *J Soc Leather Technol. Chem.***,** 82, 64-71.

Covington , A.D. and Song, L. (1999). Proceedings of XXV IULTCS Congress, p 153.

D'Aquino A, Barbani N, D'Elia G,Lupinacci D, Navigella B., Seggiani M, Tomaselli M., Vitolo S. (2004). Combined Organic Tanning Based on Mimosa and Oxazolidine:Development of Semi-Industrial Scale Process for High-Quality Bovine Upper Leather. *J Soc Leather Technol. Chem*., 88, 47-55.

DasGupta, S.(1977). Oxazolidine as tanning agent, *J Soc Leather Technol. Chem.* 61, 97-105.

Fatima, N.N.; Chandrabose, M.; Araviadhan, R.; Rao, J.R.; and Nair, B.U. (2005). Iron Phosphonium combination tanning: Towards a win-win approach. *J. Am. Leather Chemists Assoc.* 100,273-281.

Gasmelseed, G. A. and Mulla, T. H. A (1976). Simulation of continuous counter-current leaching of garad ods., *J. Appl. Chem. Biotechnol.*, 26, 618-622.

Gill, G.E.(1985). Oxazolidine, *J Soc Leather Technol. Chem.***,** 69, 99.

Gratacos, E.; Marsal, A. and Fort, M. (1993). Combination tannage with vegetable and aluminium salts: Glace kid for ladies shoe uppers. *J Soc Leather Technol. Chem.***,** 77,167.

Gunasekaran, A.; and Balsubrmanian, K.(1988). Studies on 1,3–oxazolidine and 3-hydroxyethyl-1,3-oxazolidine as tanning agents. *J Soc Leather Technol. Chem.***,** 72, 25.

Hayes, R.B. (1982). Carcinogenic effects of chromium in Biological and Environmental Aspects of Chromium. *Elsevier*, 221-247

IUP 2 (2000). Sampling *J Soc Leather Technol. Chem.***,** 84, 303-309.

IUP 36 (2000). Measurement of leather softness. *J Soc Leather Technol. Chem.***,** 84,377.

IUP 6 (2000). Measurement of tensile strength and percentage elongation. *J Soc Leather Technol. Chem.***,** 84, 317–321.

IUP 8 (2000). Measurement of tear load – double edge tear. *J Soc Leather Technol. Chem.***,** 84,327-329.

Katz S.A. and Salem H. (1994). The Biological and Environmental Chemistry of Chromium. New York: VCH Publishers. 32-37.

Kitty QU, Jeff Yang and Patrick Brutto, (2008). Oxazolidines – the versatile leather tanning agents. Angus Chemical Company, a Subsidiary of Dow Chemical Company *Leather*, 38-40.

Lu, Z.,Liao, X. and Shi, Bi. (2003). *J Soc Leather Technol. Chem.***, 87**, 173 -179.

Madhan, B., Gunasekaran, S., Narasimman, R., Rao, J. R., Sadulla, S. (2005). Integrated Free Upper Leather Processing-Part-II: Standardization and Evaluation of Vegetable-aluminium Tanning System,, *J. Am. Leather Chemists Assoc.*100, 373-379.

Madhan, B.; Aravindhan, R.; Ranjithakumar, N.; Venkiah, V.; Rao, J.R.; and Nair, B.U (2007). Combination tanning based on Tarra: An attempt to make chrome-free garment leathers. *J. Am. Leather Chemists Assoc.*, 102,198-204.

McLaughlin, G.D. and Theis, E.R.(1945).The chemistry of leather manufacture, Reinhold Publishing Corp., New York, p. 133.

Musa A.E., and Gasmelseed, G.A. (2012), Upgrading of rural garad-tanned crust leathers. J. Soc. Leather Technol. Chem. 96, 27-31.

Official Methods of Analysis (1965). Soc.Leather Tech. Chem. U.K.

Plavan, V., Valeika, V., Kovtunenko, O., Širvaitytė, J. (2009), THPS Pretreatment before tanning (chrome or nonchrome), *J Soc Leather Technol. Chem.***,** 93, 186-192.

Rahman, Mohammed A. (1995). Oxazolidine and hetero hydro oxazine azide surfactants US patent, 5, 562, 865(LL 544-470, CIID3/28) Chemical Abstract, Vol125, No. 24, Abs. No: 303849

Ramasami T, Nair BU, Kanthimathi M. and Ranganathan, C.K. (1995), Factors controlling electron transfer reactions and stabilisation of uncommon oxidation states of chromium . Proc Indian Acad Sci , 107, 411 - 422.

Ramasami, T., and Prasad, B.G.S. (1991), Environmental aspects of leather processing, Proceedings of the LEXPO-XV, Calcutta, 43-71.

Rosca, I., Sutiman, D., Crudu, M., Sibieseu, D., Cailean, A., Vizitiu, M., Apostolescu, G. (2008), Study on new complex compounds of Ti(IV) and Zr(IV) in aqueous solutions: synthesis, stability and application in cleaner technologies of natural leather, *Environ. Eng. Mang. J.*, 7, 241-248.

Saravanabhavan, S., Fathima, N. N., Rao, J. R., Nair, B.U (2007). Combination of white minerals with natural tannins chrome-free tannage for garment leathers, *J Soc Leather Technol. Chem.***,** 91, 154-158.

Shi, Youle HE, Hoajun Fan, Shaoyu Zeng, A.D, Covington and G.E. Attenburrow, (1999). High stability organic tanning using plant polyphenols. Parts 2. The mechanism of the vegetable tannin-oxazolidine tannage. *J Soc Leather Technol. Chem.***,** 83, 8-13.

SLP 9 (IUP 9) official method of analysis, (1996). Measurement of distension and strength of grain by the ball burst, In Official methods of analysis. *The Society of Leather Technologist and Chemists*, Northampton.

Snow ET. (1994). Effects of chromium on DNA replication *in vitro*. Environ Health Perspect, 102 (suppl. 3): 41-44.

Sugiyama M. (1992), Role of physiological antioxidants in chromium (VI)-induced cellular injury. *Free Radic. Biol. Med.*, 12,397-407.

Sundarrajan, A.; Madhan, B.; Rao J.R.; and Nair, B.U. (2003). Studies on tanning with zirconium oxychloride: Part I Standardization of tanning process. *J. Am. Leather Chemists Assoc.*, 98,101-106.

Zhao Ya-Ting and Wang Xue-Chuan (2007). Chinese developments chrome-free and low-chrome tanning materials. *J Soc Leather Technol. Chem.***,** 91,246.