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Research Article

Quebracho - Oxazolidine Combination Tanning for Leather Making

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Abstract

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. 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. Combination tannages are considered as suitable alternatives for a chrome-free tanning system. Among the innumerable combination tannages that are currently being exploited are vegetable tannin/oxazolidine combinations as the most promising options. In this study, organic combination tanning process based on quebracho powder (Schinopsis balansae) and oxazolidine for the production of upper leathers is presented. Quebracho powder has been utilized in the combination tanning system with oxazolidine. Quebracho tanned leathers from goat skins used as control leathers. It has been observed that Quebracho - oxazolidine combination tanning which employs 20% Quebracho and 5% oxazolidine provides a shrinkage temperature of 102°C, which is 18°C more than the control leathers. The characteristics of the leathers indicate that the Quebracho -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 upper leathers using combination of Quebracho and oxazolidine suggest that this tannage is a promising alternative to traditional chrome tanning.

***Keywords**: Combination tannage, Quebracho, Oxazolidine, Chrome free*

1. Introduction

Leather industry is making significant contributions to economic development, however it is globally facing challenges owing to pollution it causes to the environment (George N. *et al*., 2014; Saran S. *et al*., 2013; Jia L. *et al*., 2016). Tanning is a conversion process of rawhide to a stable material that dries out to a form without putrefying and becomes suitable for a variety of end applications (Kanth, *et al*., 2009; Krishnamoorthy, *et al*., 2012). Compared with different kinds of tanning agents, chrome tanning agent still plays a dominant role in leather-making industry for the time being, which can show nice handing quality, high hydro-thermal stability, good physical and mechanical strength and less consuming time. And these good properties cannot be achieved by other tanning materials, though chrome-tanned leathers were produced only several decades in commercial scale (Dixit, *et al*., 2015). The pollution problems of trivalent chromium (Cr(III)) in waste are due to insufficiency of the treatment systems and formation of hexavalent chromium (Cr(VI)), carcinogenic and mutagenic, which led to the search for an eco-friendly greener option to tanning process (Kolomaznik *et al*., 2008).

More than 90% of the global leather production is currently through chrome-tanning process (Li *et al*., 2009; Saadia *et al*., 2009). However, the uptake of chromium during the traditional chrome tanning process is only 65-75% (Ganesan *et al*., 2013; Sundarapandiyan *et al*., 2011), that is to say, 25-35% of the chromium remains in tanning liquor. A large quantity of chrome liquors discharged into the soil and water may cause serious pollution (García *et al*., 2013; Bonilla *et al*., 2010; Morera *et al*., 2011). A lot of research has been carried out in order to explore how to minimize chrome tanning impact including work on: chrome-free and higher exhaustion chrome tanning

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systerm. Chrome-free system can completely abandon the use of chrome tanning agents, and solve the problem of chromium pollution from the source. In the previous study, vegetable tanning agents (Lu *et al*., 2005), aldehydes, metal combination tanning agents (Su *et al*, 2005), syntans (Li, *et al*, 2004) and oil tanning agent (Sundar, *et al*., 2004) were mainly researched as chrome-free tanning agents.

Vegetable tannins are polyphenolic substances that can be easily extracted with water from almost all plants (Solomons and Fryhle, 2015) and have traditionally been used to tan leather (Falcão and Araújo, 2013; Venter *et al*., 2012). Tannins are a heterogeneous group of polyphenols widely present in the plant kingdom as secondary metabolites for protective purposes, with molecular weight between 500 and 3,000 Da (Falcão and Araújo, 2014). They occur in bark, wood, fruits, fruit pods, leaves, roots, and plant galls (Mané *et al*., 2007; Ricci *et al*., 2015). Tannins are classified into hydrolysable and condensed tannins (Radebe *et al*., 2013). The hydrolysable tannins are composed of a polyol central core acylated by a variable number of gallic or ellagic acid units and derivatives (Falcão and Araújo, 2013, 2014;Mané *et al*., 2007; Radebe *et al*., 2013). The condensed tannins, also called proanthocyanidins are oligomers and polymers formed in the flavan-3-ol basic structure, viz., quebracho (Fig 1) and mimosa (Fig 2) are condensed tannins (Falcão and Araújo, 2013; Mané *et al*., 2007; Radebe *et al*., 2013; Ricci *et al*., 2015; Venter *et al*.,2012).

Oxazolidines, heterocyclic derivatives obtained by the reaction of aminohydroxy compounds with formaldehyde, (Dasgupta, 1977; Gill, 1985) are an alternative to aldehyde tannage. Under hydrolytic conditions, the rings open to form an Nhydroxymethyl compound, which can react with one or more amino groups to produce effective cross-linking. (Dasgupta, 1977) Oxazolidines have been shown to possess high reactivity and good tanning ability. Oxazolidine will react with the amino groups of collagen to form cross-links improving the shrinkage temperature of leather (Dasgupta, 1977; Gunasekaran,1988).

Leather tanned by oxazolidine E has a similar shrinkage temperature to that of glutaraldehyde tanned leather, (Dasgupta, 1977) but is less full and less hydrophilic, because the molecular weight of monomeric oxazolidine is smaller than that of polymerized glutaraldehyde. 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 (Biokemica technical data sheet) .

Quebracho is a tree indigenous to South America, the best wood for tannin being found in the Gran chaco district in the North of Argentina, and Uruguay. Both bark and heart woods contain tannin and the average tannin contents are as follow: Heart wood 14-26 % ;Bark 22-45% . Extracts are generally manufactured from wood. The wood is so hard and heavy that it sinks in water. In fact, the name quebracho , is derived from two Portuguese words meaning “axe breaker”. Under the name, Quebracho, come several types of trees but the important species are as follow: Quebracho Colorado (*Schinopsis.balansae*.) and Quebracho Maco (*Schinopsis.Lorentzii*) (Dutta 1999). Ordinary or insoluble Quebracho is the name given to the extract prepared by concentrating the hot water extractives. This untreated solid extract has a very low salt content and contains little natural solid-so that a liquor of 50^{o}BK strength has a pH value of about 4.6. This ordinary Quebracho is therefore an ideal material for sole leather manufacture at the last stage in hot pits (Dutta 1999, Sarkar 2005). Sulphited quebracho on the other hand is soluble in cold water and its rate of penetration is high, sludge formation is low, colour of the leather produced is very light etc. This type of modified quebracho produces very soft type of leather and so for medium hard leather semi soluble quebracho, produced by using limited quantity of sulphite and bisulphate mixture during chemical modification, is therefore recommended .As a tanning material it belongs to the catechol class (Dutta 1999, Sarkar 2005). The condensed tannins are polymerized catechin subunits and are found in nature with varying degrees of polymerization and are also known as polymeric proanthocyanidins. Since the quebracho extract contains polyphenolic compounds 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.

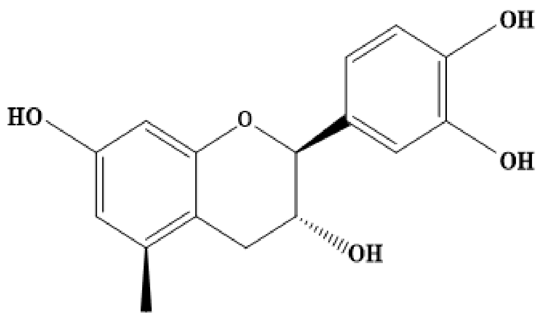

Fig. 1 Quebracho Tannin

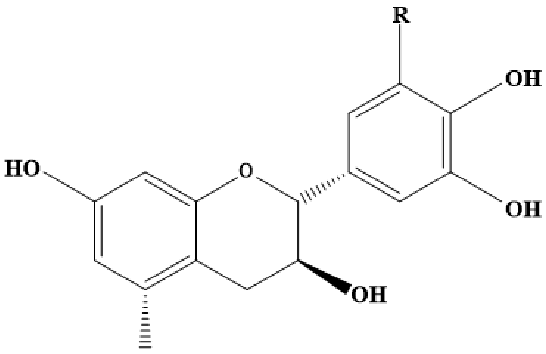

Fig. 2 Mimosa Tannin

2. Materials and Methods

Materials

Conventionally processed pickled goats skins were taken for the combination tanning trials. Quebracho powder used as condensed tannin in the combination trials 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.

Tanning Trials

The tanning experiments were carried out on pickled goat skins. Experimental combination tanning trial oxazolidine followed by Quebracho (Oxaz-Quebracho) were carried out as per the process mentioned in Table 1 and combination tanning based on Quebracho followed by oxazolidine (Quebracho-Oxaz) was carried out as per the process mentioned in Table 2. Control Quebracho tanning trial was carried out as per process given in Table 3. Both experimental and control leathers were processed into upper crusts following the post –tanning process mentioned in Table 4.

Determination of shrinkage temperature

The shrinkage temperature of both control and experimental leathers were determined using the Theis shrinkage tester (McLaughlin and Thesis 1945). 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.

Table 1 Formulation of Oxaz-Quebracho Combination Tanning Process for Goat 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	
	2	Phenolic syntan	30	
	10	Quebracho	120	
	10	Quebracho	120	
Fixing	0.5	Formic acid	3 × 10 + 30	Check the pH to be 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 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 (IUP 2 2000). 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, (IUP 6 2000) grain crack strength (SLP 9 1996) and tear strength (IUP 8 2000) were measured as per standard procedures. Each value reported is an average of four (2 along the backbone, 2 across the back bone) samples.

Table 2 Formulation of Quebracho-Oxaz 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	Phenolic syntan	30	
	10	Quebracho	120	
	10	Quebracho	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 1.2 mm. The shaved weight noted.

Table 3 Formulation of Quebracho 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	Phenolic syntan	30	
	10	Quebracho	120	
	10	Quebracho	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 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 (Clesceri, *et al* 1989).

Chemical Analysis of leathers

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 trials using Quebracho and oxazolidine (Biotan G100) were carried out with 5% offer of oxazolidine and 20% offer of Quebracho. The shrinkage temperature data of leathers tanned with Quebracho - Oxaz and Oxaz-Quebracho combination along with Quebracho control is given in Table 5. From the table it is seen that both the combination resulted in leathers with good shrinkage temperature. The shrinkage temperature of leathers obtained from Quebracho-Oxaz combination tanning is slightly higher than Oxaz-Quebracho. However, both the combination tanning resulted in leathers with shrinkage temperature greater than 95°C, which are better than control leathers from Quebracho of Ts 84°C.

Table 4 Formulation of Post-tanning Process for Making Upper Crust Leathers

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

Ecological Impact - spent liquor analysis

The spent liquor from control and experimental processes contains highly organic matter and it contributes to extremely high COD, dissolved and suspended. 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 6. 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 Quebracho tanning (control). The BOD_5 and TDS of the spent liquor processed from Quebracho and Oxaz combination tanning trials have significantly reduced compared to the spent liquor of control Quebracho tanning trial.

Table 5 Shrinkage temperature of crust leathers for experimental and control

Experiment	Shrinkage temperature, Ts (°C)
Oxaz- Quebracho	95±1
Quebracho -Oxaz	102±2
Quebracho (Control)	84±0.5

Table 6 Characteristics of spent liquor for experimental and control

Experiment	COD (mg/l)	% reduction in COD	BOD_5 (mg/l)	% reduction in BOD	TDS (mg/l)	% reduction in TDS
Quebracho (control)	120900±3050	-	52000±1050	-	98200±1600	-
Oxa- Quebracho	106300±2500	12	34000±1200	34.62	78500±1300	20
Quebracho - Oxa	97800±1800	19	29000±1100	44.23	64300±1700	34.52

Tactile properties of crust leathers for experimental and control

The organoleptic properties (visual assessment) of upper crust leathers for experimental and control are given in Fig. 3. (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 Quebracho tannage. The organoleptic properties of the Quebracho- Oxaz crust leathers are slightly better compared to Oxaz-Quebracho crust leathers.

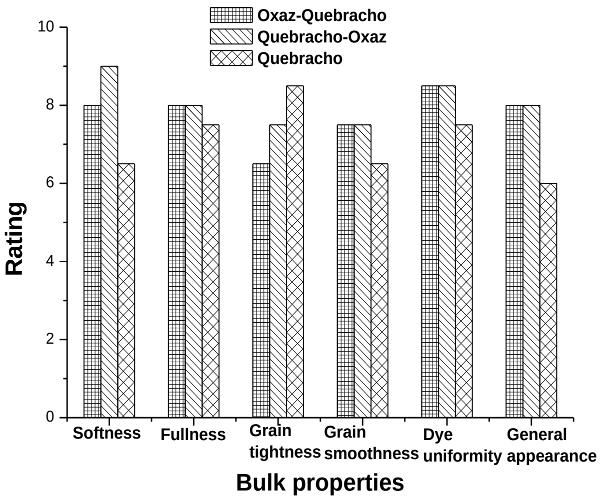

Fig. 3 Graphical representation of organoleptic properties of the Experimental and control leather

Strength characteristics of experimental and control crust leathers

The physical strength measurements of experimental and control leathers are given in Table 7. The physical strength measurements viz., tensile strength, tear strength has been found to be better for experimental leathers. The experimental Quebracho-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. 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 Quebracho control leathers.

Table 7 Physical strength characteristics of experimental and control crust leathers

Parameter	Oxaz-Quebracho	Quebracho -Oxaz	Quebracho (control)	BIS standards
Tensile strength (Kg/cm^2)	225±2	255±2	215±3	200
Elongation at break (%)	57±0.8	59±1.7	55±1.5	40-65
Tear strength (Kg/cm)	54±1.6	68±1.6	50±0.8	30
Load at grain crack (kg)	25±0.6	27±0.6	23±0.6	20
Distention at grain crack (mm)	11±0.6	12±0.6	10±0.6	7

Chemical Analysis of the crust leather

The chemical analysis values of experimental crust leathers (Oxaz-Quebracho and Quebracho-Oxaz) and control (Quebracho) are given in Table 8. 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 8 Chemical Analysis of experimental and control crust leathers

Parameter	Quebracho (control)	Oxaz-Quebracho	Quebracho - Oxaz
Moisture %	13.15	13.90	13.15
Total ash content %	2.75	2.25	2.30
Fats and oils %	3.45	2.45	2.50
Water soluble matter %	5.20	2.75	3.45
Hide substance %	52	53	52
Insoluble ash %	1.25	1.35	1.30
Degree of tannage %	47.98	50.10	53.10

Conclusion

Combination tannages are thus considered as suitable alternatives for a chrome-free tanning system. Among the innumerable combination tannages that are currently being exploited are vegetable tannin/oxazolidine and vegetable tannin/aluminium tanning agent combinations as the most promising options. Oxazolidines have been shown to possess high reactivity and good tanning ability. Oxazolidine will react with the amino groups of collagen to form cross-links improving the shrinkage temperature of leather. In the present study, an attempt has been made to produce upper leather using combination tanning process based on Quebracho and Oxazolidine. It is seen that combination tanning system with 20% Quebracho and 5% Oxazolidine results in leathers with a maximum shrinkage temperature of 102°C, which is 18°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 Quebracho -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 upper leathers from Quebracho -Oxaz combination with a shrinkage temperature of 102°C.

References

Biokemica technical data sheet: BIOTAN G100 Heterocyclic synthetic tanning agent.

Bonilla, S.H., Almeida, C.M.V.B., Giannetti, B.F., Huisingh, D., (2010). The roles of cleaner production in the sustainable development of modern societies: an introduction to this special issue. J. Clean. Prod. 18, 1-5.

Clesceri. LS, Greenberg AE, Trussel RR.Eds. (1989) In standard methods forthe examination of water and wastewater, 17th ed, American public health association Washington DC.

Dasgupta, S., Oxazolidine as tanning agent. J. Soc. Leather Technol. Chem., (1977), 61, 97.

Dixit, S., Yadav, A., Dwivedi, P. D., Das, M., (2015). Toxic hazards of leather industry and technologies to combat threat: a review. Journal of Cleaner Production 87, 39-49.

Dutta, S.S (1999). Vegetable tanning, In Principles of Leather Manufacture, 369-374.

Falcão, L., Araújo, M.E.M., (2013). Tannins characterization in historic leathers by complementary analytical techniques ATR-FTIR, UV–vis and chemical tests. J.Cult. Herit. 14, 499–508.

Falcão, L., Araújo, M.E.M., (2014). Application of ATR?FTIR spectroscopy to the analysis of tannins in historic leathers: the case study of the upholstery from the 19th century Portuguese Royal Train. Vib. Spectrosc. 74, 98–103.

Ganesan, K., Sayeed, S., Praveen, K.S., (2013). Greener approach to leather tanning process: D-Lysine aldehyde as novel tanning agent for chrome-free tanning. J. Clean. Prod. 42, 277-286.

García, V., Steeghs, W., Bouten, M., (2013). Implementation of an eco-innovative separation process for a cleaner chromium passivation in the galvanic industry. J. Clean. Prod. 24, 1-10.

George, N., Chauhan, P. S., Kumar, V., Puri, N., Gupta, N., (2014). Approach to ecofriendly leather: Characterization and application of an alkaline protease for chemical free dehairing of skins and hides at pilot scale, J. Clean. Prod. 79, 249–257.

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

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

IUP 2. (2000); Sampling. JSLTC 84, 303.

IUP 6. (2000); Measurement of tensile strength and percentage elongation. JSLTC 84, 317.

IUP 8. (2000); Measurement of tear load – double edge tear. JSLTC 84, 327-329.

Jia L, Ma J, Gao D Bin Lyu, Jing Zhang., (2016). Application of an amphoteric polymer for leather pickling to obtain a less total dissolved solids residual process[J]. J Clean Prod. 139:788-795.

Kanth, S. V., Venba, R., Madhan, B., Chandrababu, N., Sadulla, S., (2009). Cleaner tanning practices for tannery pollution abatement: role of enzymes in eco-friendly vegetable tanning. Journal of Cleaner Production 17, 507-515.

Kolomaznik, K., Adamek, M., Andel, I., Uhlirova, M., (2008) . Leather waste-potential threat to human health, and a new technology of its treatment. Journal of Hazardous Material 160, 514-520.

Krishnamoorthy, G., Sadulla, S., Sehgal, P., Mandal, A. B., (2012). Green chemistry approaches to leather tanning process for making chrome-free leather by unnatural amino acids. Journal of hazardous materials 215, 173-182.

Li L. X., Huang, Z., Pan, T., *et al*, (2004). Study on the cloud point of aqueous mixtures of cationic and anionic surfactants [J]. Chemical Research and Application. 16 (2):90-291.

Li, K., Chen, H., Wang, Y., Shan, Z., Yang, J., Brutto, P., (2009). A salt-free pickling regime for hides and skins using oxazolidine. J. Clean. Prod. 17, 1603-1606.

Lu, Z., Liao, X., Zhang, W., *et al*, (2005). Mechanism of vegetable tannin-aldehyde combination tannage [J]. J. Am. Leather Chem. Assoc. 100: 432-437.

Mané, C., Sommerer, N., Yalcin, T., Cheynier, V., Cole, R.B., Fulcrand, H., (2007). Assessment of the molecular weight distribution of tannin fractions through MALDI-TOF MS analysis of protein-tannin complexes. Anal. Chem. 79, 2239–2248.

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

Morera, J.M., Bartoli, E., Chico, R., (2011). Minimization of the environmental impact of chrome tanning: a new process reusing the tanning floats. J. Clean. Prod. 19, 2128-2132.

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

Radebe, N., Rode, K., Pizzi, A., Giovando, S., Pasch, H., (2013). MALDI-TOF-CID for the microstructure elucidation of polymeric hydrolysable tannins. J. Appl. Pol. Sci.128, 97–107.

Ricci, A., Olejar, K.J., Parpinello, G.P., Kilmartin, P.A., Versari, A., (2015). Application of fourier transform infrared (FTIR) spectroscopy in the characterization of tannins. Appl. Spectrosc. Rev. 50, 407–442.

Saadia, R.T., Munir, H.S., Nazia, S., (2009). Comparative statistical analysis of chrome and vegetable tanning effluents and their effects on related soil. J. Hazard. Mater. 169, 285-290.

Saran, S., Mahajan, R. V., Kaushik, R., Isar, J., Saxena, R. K. (2013). Enzyme mediated beam house operations of leather industry: a needed step towards greener technology. J. Clean. Prod. 54, 315-322.

Sarkar K.T (2005)., Vegetable tanning, in Theory and Practice of Leather Manufacture, 230-231.

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

Solomons, T.W.G. and Fryhle, C., (2015). Química Orgânica, vol. 2. (8th Ed.), 2004, Rio deJaneiro: editora LTC. Tondi G. and Petutschnigg A., Middle infrared (ATRFT-MIR) characterization of industrial tannin extracts. Ind. Crop. Prod. 65,422–428.

Su, X. X., Wang, X. Ch., (2005). The synthesis and application of acrylic resin-Al complex tanning agent [J]. China Leather, 34 (3): 53-56.

Sundar, V. J., Vedaraman, N., Balakrishanan, P., *et al*, (2004), Chamois leathers: An approach for accelerated oxidation [J]. J. Soc. Leather Tech. Ch. 88 (6): 256-25.

Sundarapandiyan, S., Brutto, Patrick E., Siddhartha, G., (2011). Enhancement of chromium uptake in tanning using oxazolidine. J. Hazard. Mater.190 (1-3), 802-809.

Venter, P.B., Sisa, M., van der Merwe, M.J., Bonnet, S.L., van der Westhuizen, J.H.,(2012). Analysis of commercial proanthocyanidins. Part 1: the chemical composition of quebracho (Schinopsis lorentzii and Schinopsis balansae) heartwood extract. Phytochemistry 73, 95–105.