Combination Tanning Based on Tara: An Attempt to Make Chrome--Free Garment Leathers

by

B. Madhan*, R. Aravindhan, N. Ranjithakumar, V. Venkiah, J. Raghava Rao*, B. Unni Nair

Chemical Laboratory and Centre for Human and Organizational Resources Development

Central Leather Research Institute

Adyar, Chennai -600020, India

Abstract

Presently, there is rising demand for the manufacture of chrome-free leathers. In this work, an attempt has been made to manufacture chrome-free garment leathers using a combination tannage based on tara tannin and co-tanning adjuncts viz., aluminum and gluteraldehyde. The shrinkage temperature of leathers using different combinations of tara and aluminum/ gluteraldehyde were found to be around 90°C. Tara-aluminum combination tanning system resulted in leathers with less softness and grain smoothness compared to tara-gluteraldehyde combination tanning system. The order of addition of gluteraldehyde had a significant influence on the organoleptic properties of the leathers. Gluteraldehyde pretreatment of tara tanned leathers gave better results when compared to post treatment. Tara at the 8% level was found to be optimum for combination tanning using 2% gluteraldehyde pretreatment. The gluteraldehyde-tara tanning system resulted in white leathers compared to the undyed chrome tanned crust leathers. The physical, organoleptic, dyeability and finishing characteristics of the crust leathers from both control and gluteraldehyde-tara tanning were comparable.

Abstracto

Actualmente, hay demanda creciente para la fabricación de cueros libres de cromo. En este trabajo, se ha llevado a cabo una propuesta para fabricar cueros libre de cromo para vestimenta usando un curtido combinado basado en tanino de tara y curtición adjunta con aluminio y glutaraldehído. La temperatura de contracción de cueros usando diversas combinaciones de tara y aluminio/glutaraldehído estuvieron alrededor de 90°C. El sistema de curtido combinando Tara-Aluminio dio lugar a cueros con menos suavidad y lisura de flor comparado con el sistema combinando tara-glutaraldehído. El orden en la adición del glutaraldehído tuvo una influencia significativa en las características organolépticas de los cueros. El tratamiento previo con Glutaraldehído sobre cueros curtidos con tara dio mejores resultados que empleado como tratamiento posterior. La oferta de 8% de Tara se encontró como óptima con un pre-tratamiento de glutaraldehido del 2%. El sistema de curtición glutaraldehido-tara dio lugar a cueros blancos comparados con cueros crust curtidos al cromo sin teñir. Las características físicas, organolépticas, de tingibilidad y acabado de los cueros semi-terminados de las muestras control y de las curtidas con glutaraldehído-tara son comparables.

Introduction

Present day research is focused on eco-friendly products and processes. The comprehensive concern on the negative impact of the leather industries on the environment has forced tanners to pay attention to processes that would reduce the problems related to pollution. To overcome the problems associated with chrome tanning[1-5], researchers throughout the world are looking for alternative tanning systems. As mentioned by Covington, any alternative tanning system developed should provide leathers with good hydrothermal stability, strength characteristics, organoleptic properties and most importantly the product should be ecobenign.[6] In this scenario, vegetable tannin owing to its natural origin, is considered to be an eco-friendly option. Although the vegetable tanning system enjoys a few advantages, it suffers from certain drawbacks such as providing fuller leathers and difficulty in making pastel shades. To overcome these constraints, tara, a condensed tanning agent has been chosen. This tanning agent provides lighter shades and also due to its low astringency and loading nature, can be used in the manufacture of garment leathers. Tara tannin as a solo-tanning agent may not be effective for the manufacture of garment leather. Hence, in this work the use of vegetable based combination tanning has been studied along with suitable co-tanning adjuncts.

Tara is the name commonly given for a fairly well known material, which consists of the dried pods of *Caesalpinia spinose*, a tree or shrub. The pods are similar to divi-divi and algarrobilla and all three belong to the same genus. The tannin content of tara varies from 30-35%. Tara has been used mainly for tanning light leathers. Aluminum is one of the potential adjuncts for vegetable tanning. Aluminum tannage fulfills separation of the skin fiber to obtain an opaque and supple material after drying. The ability of aluminum to serve as a tanning agent has been explored previously by many workers.[7-9] Aluminum salts differ from chrome salts in that they give white leathers and are not firmly fixed to the fiber. Aluminum tanning agents have quite high astringency and one of its outstanding merits is its ability to tighten the fiber structure, either to give a finer grain or a tighter nap on suede leathers, when used along with chrome tanning salts. Attention has been drawn already towards aluminum tannage as a replacement for chromium tanning due to greater acceptability of alum salts in tannery effluents. Aluminum-mimosa combination has been found to give shrinkage temperature of about 100°C. Also, aluminum produces wet white leathers, which is ideal for pastel shades in garment leathers and richer dyeing in upper leathers. Aluminum improves the color of vegetable tanned leather and imparts a light color to the final leather. Vegetable tannage followed by basic aluminum has been found to produce leather with remarkable hydrothermal stability.

Gluteraldehyde, one of the simplest dialdehyde is also a potential adjunct co-tanning agent for vegetable tanning. Gluteraldehyde, as a tanning agent increases the shrinkage temperature by providing additional cross-linking (bifunctional nature). When used as a solo-tanning agent, it can produce good leathering effect. The application of gluteraldehyde as a supplementary tannage to chrome tannage has resulted in greater stabilization of the protein fiber, which results in raising the shrinkage temperature and a greater resistance of the leather to chemical attack. Gluteraldehyde provides softening effect on leather and also the ability to make water repellency and other specific effects like perspiration resistance.[12]. In this work, a combination tanning employing aluminium - tara and gluteraldehyde - tara has been attempted as an alternative chrome-free tanning system for making garment leathers.

Experimental

Materials

Conventionally processed pickled sheepskins were taken for the tanning trials. All the chemicals used were of commercial grade and detailed in an appended note.

Combination Tanning Trials

Two combination tanning systems (Ta-Al and Ta-Gl) have been adopted in this study for the manufacture of garment leathers from pickled sheepskins. Two pickled sheepskins were used for each tanning trials. Combination tanning trials with tara and aluminum/gluteraldehyde were carried out by altering the order of addition of the tanning agents. For all the tanning trials, the % chemicals offered was based on limed pelt weight.

Gluteraldehyde-Tara combination tanning

Trial 1: (Ta-Gl) The pickled sheepskins were adjusted to pH 4.5 using sodium bicarbonate and the following tanning process was adopted. Water- 100% and tara - 12% were offered to the pelts and the drum was run for 180 minutes. Then 2% Relugan GT 50 was added and the drum was run for 120 minutes. The final pH of the leather was found to be 4.0-4.2. The leathers were then piled for 24 hrs.

Trial 2: (Gl-Ta) The pickled sheepskins were adjusted to pH 4.5 using sodium bicarbonate and the following tanning process was adopted. 100% water and 2% of Relugan GT 50 were offered to the pelts and drummed for 120 minutes. Then 12% tara was offered and the drum was run for 180 minutes. The final pH of the leather was found to be 4.0-4.2. The leathers were then piled for 24 hrs.

Aluminum -Tara combination tanning

Trial 3: (Ta-Al) The pickled sheepskins were adjusted to pH 4.5 using sodium bicarbonate and the following tanning

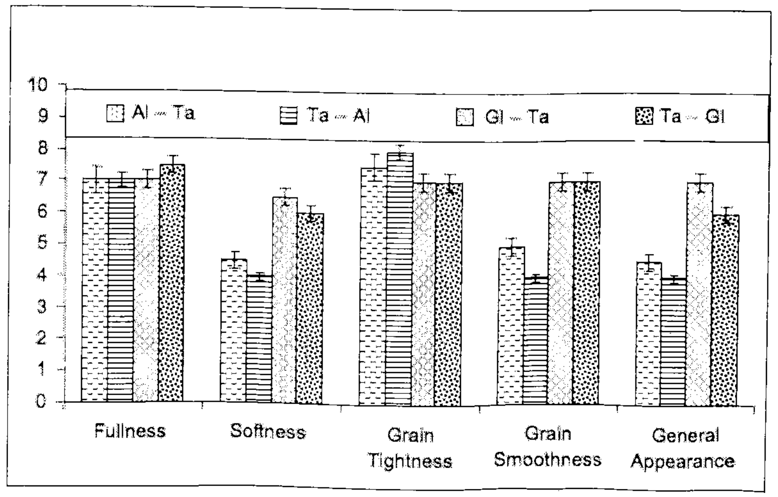

Figure 1. Organoleptic properties of the nappa crust leathers processed employing tara based combination tanning systems

* Correspondence Author - Fax: +91 44 24911589; Tel: +91 44 24411630,
E-mail: clrichem@mailcity.com

Manuscript received September 14, 2006, accepted for publication February 12, 2007

TABLE I
Post Tanning Recipe for Garment Leather

Process	Chemical	%	Duration (min)	Remarks
Neutralization	Water	200		(% chemicals are based
	Sod formate	1.5		on shaved weight)
	Sellasol NG	1	30	
	Sod bicarbanate			pH adjusted to 5.3 - 5.5
	(1:10 with water)	.75	3 x 20 + 30	Drain, wash
Retanning	Relugan RE	2		
	Basyntan DI	3		
	Tergotan RPF-IN liq	3	90	Check exhaustion
Fatliquoring	Derminol FS-IN liq	1		
	Balmol SXE	1		
	Balmol SX-20	3	120	Check exhaustion
Fixing	Water	50		Drain/wash/ pile over night.
	Formic acid	2	30	Next day - set, hook to dry, stake, shave, buff, trim and dry drum
Wet back	Water	200		% chemicals based
	Luwet 40	1		on crust weight
	Liquor ammonia	0.5	60	pH adjusted to 5.3 - 5.5
Retanning and fatliquoring[1]	Tanicor R5-IN p	3		
	Softimol liquor nappa	2		
	Kroatan RS8	4		
	Kroatan 477	3		
	Softimol licker nappa	7		
	Fospho licker S	4		
	Lipoderm liquor 2FB	4	2 x 45	Check exhaustion
Fixing	Water	50		
	Formic acid	2	2 x 20	Check exhaustion

[1] For dyeability studies, 8% of acid black dye (based on crust weight) has been used at this stage

process was adopted. Water -100% and 12% of tara was offered to the pelts and the drum was run for 180 minutes. Then 4% Balsyn Al was added and drummed for 120 minutes. The final pH of the leather was adjusted to 4.0 using sodium bicarbonate. The leathers were then piled for 24 hrs.

Trial 4: (Al-Ta) The pickled sheepskins with 80% of pickle liquor were offered 4% of Balsyn Al and drummed for 120 minutes. The pH of the bath was adjusted to 4.0-4.5 using sodium bicarbonate. Then 12% of tara was offered to the pelts and the drum was run for 180 minutes. The final pH of the leather was adjusted to 4.0. The leathers were then piled for 24 hrs.

For leathers tanned from Trials 1 to 4, the hydrothermal stability was measured by using a Theis shrinkage tester.[11] The average values of two measurements for four experimental leathers of each trial was calculated and reported along with standard error. The leathers were then sammed and shaved to required thickness of 0.8 mm. The leathers were post tanned using the process mentioned in Table I.

Optimization of the Amount of Tara

Experimental trials varying the amount of tara offer were carried out using the tanning process mentioned in Trial 1. The amount of tara used was varied as 6, 8, 10 and 12% and subsequently the leathers were post tanned using the process mentioned in Table I.

Matched Pair Comparison of Garment Leathers Employing Gl-Ta and Chrome Tanning

Three left halves of pickled sheepskins were tanned with 8% tara using Gl-Ta combination tanning system as mentioned in Trial 1. The matched pair right halves of the pickled skins were chrome tanned following a conventional process using 8%

TABLE II
Finishing Recipe for Garment Leathers

Process	Chemicals	Quantity (g/L)	Remarks
Base coat	Rodobind 4080	50	
	Rodobind EP34	50	
	Rodobind 8727	30	
	Rodobind R577	30	
	Rodowax 619	30	
	Pigment	50	
	Dye solution	10	6 x coats, plain plate (100 kg/cm2)
Anionic clear coat	ALPA UT	100	
	ALPA 511	50	
	ALPA EP19	60	
	Q wax 80	30	2 x coats,
Fixing	ALPA tan BTX	1:2 with water	2 x coats dry milled for 2 hrs, toggled
Top coat	GW4	50	
	Sensol SW	10	2 x coats, plain plate (100 kg/cm^2)

TABLE III
Shrinkage Temperature of Leathers Processed Using Tara-Aluminium and Tara-Gluteraldehyde Tanning Systems

Tanning System	Order of Addition	Shrinkage Temperature (oC)
Tara - Aluminium	Aluminium followed by Tara (Al - Ta)	90±1
	Tara followed by Aluminium (Ta - Al)	93±2
Tara - Gluteraldehyde	Tara followed by Gluteraldehyde (Ta - Gl)	90±1
	Gluteraldehyde followed by Tara (Gl - Ta)	92±1

TABLE IV
Organoleptic Properties of Crust Leathers Tanned Using Increasing Offer of Tara Powder

% Tara Offer	Grain Tightness	Softness	Grain Smoothness	General Appearance
6	6	8	8	7
8	6.5	8	7.5	7.5
10	6.5	7.0	7.5	6.5
12	7.0	6.0	7.0	6.5

* Organoleptic properties evaluated by experience tanners and the values reported are found to deviate less than ± 0.5.

TABLE V
Physical Strength and the Shrinkage Temperature of Crust Leathers Tanned using Chromium and Gl-Ta Tanning

Tanning systems	#Tensile Strength (kg/cm^2)	#Tear Strength (kg/cm)	@Load at Grain Bursting (kg)	@Distension (mm)
Chrome tanning	163±15	50±8	20±2	10.2±0.3
Gl - Ta Tanning	234±18	52±10	29±1	11.5±0.5
UNIDO norms	120	20	-	-

Average of 4 samples measured (two along the backbone and two across the backbone)
@ Average of two measurements

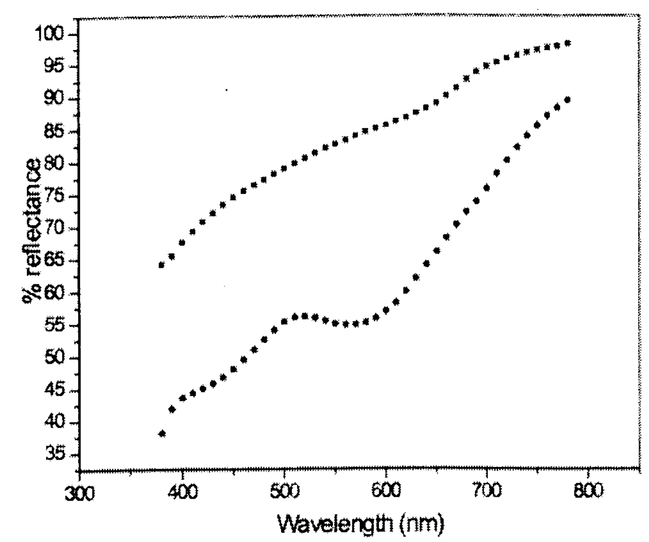

Figure 2: Reflectance spectra of crust leather processed from chromium (●) and Gl-Ta tanning (■)

TABLE VI
Comparison of Organoleptic Properties of Chrome and Gl-Ta Tanned Crust Leathers

Properties	Chrome Tanned Crusts	Gl -Ta Tanned Crusts
Softness	8.0	8.5
Grain Smoothness	8.0	8.0
General Appearance	8.0	8.5

Organoleptic properties evaluated by experience tanners and the values reported are found to deviate less than ± 0.5.

TABLE VII
Wet and Dry Rub Fastness of Finished Leathers from Control and Experimental Tanning Systems

Finished Leathers from	Wet Rub fastness	Dry Rub fastness
Chrome tanning system	3-4	4-5
Gl-Ta tanning system	3-4	4-5

TABLE VIII
Analysis of Spent Tan Liquor from Chrome and Gl-Ta tanning

Parameters	Chrome (g/kg)*	Gl-Ta (g/kg)*
COD	45±2	54±3
TS	100±5	105±4
Chromium	5.5±0.5	-

* Pollution load in g/kg of raw material processed

basic chromium sulfate salt and labeled as control leathers. Leathers from both tanning system were post tanned commonly using the post tanning recipe mentioned in Table I. Crust leathers from both the control and experimental tanning system were assessed for their organoleptic and strength properties.

Hand Evaluation of Crust Leathers

Garment crust leathers were assessed for grain tightness, fullness, softness, grain smoothness and general appearance by standard hand and visual evaluation techniques. Three experienced tanners rated the leather in a scale of 0 to 10 points for each functional property, where higher points indicate better property.

Physical Testing of Crust Leathers

The samples for physical testing were obtained as per IULTCS method.[12] Physical properties such as tensile strength, tear strength and grain crack strength were examined as per the standard procedures.[13-15]

Finishing properties of Gl-Ta Tanned Crust Leather

The control and experimental crust leathers were finished using recipe mentioned in Table II. The samples from the finished leathers were cut according to the official sampling procedure.[12] Then the leathers were subjected to the fastness testing adopting a standard procedure.[16]

Analysis of Spent Tan Liquor

Spent tan liquors from both chrome tanned control and Gl-Ta experimental processes were collected after tanning and analyzed for COD and TS (dried at 103-105°C for 1 h) as per the standard procedures.[17] From this the emission loads were calculated by multiplying concentration (mg/L) with volume of effluent (L) and presented as emission load per kg of raw skin processed.

RESULTS AND DISCUSSION

Selection of Chrome-Free Combination Tanning System for Garment Leathers

Two tanning system *viz.* Ta-Al and Ta-Gl have been identified for a possible replacement of chrome tanning system for making garment leathers. The shrinkage temperatures of leathers tanned using the two combinations with different order of additions are given in Table III. From Table III, it is observed that these combination tanning systems exhibit shrinkage temperature above 90°C. There is no significant change in shrinkage temperature on changing the order of addition of the tanning agents. However, significant changes in the organoleptic properties of the nappa crust leathers have been observed with changes in the order of addition of tanning agents (Fig. 1). Crust leathers tanned using Ta-Al combination resulted in tight and coarse leathers compared to Ta-Gl system. The crust leathers tanned with Gl-Ta were soft and smooth as compared to the leathers tanned using Ta-Gl. Hence, tara-gluteraldehyde tanning system offered in the order gluteraldehyde followed by tara (Gl-Ta) has been chosen for subsequent experimental trials.

Optimization of Tara Offer

The organoleptic properties of crust leathers tanned using various percentage offers of tara viz. 6, 8, 10 and 12 % with constant 2% gluteraldehyde pretreatment are shown in Table IV. From the table, it is clear that an offer of above 8% tara powder (based on pelt weight) affects the properties required for garment leather. The softness and overall appearance of the

garment crust leather are found to be better at 8% offer of tara powder. Hence, an offer of 8% tara has been chosen as the optimum amount in the Gl-Ta tanning system.

Comparison of the Garment Leathers Made using Gl-Ta and Chrome Tanning System

Color Shade of the Tanning System

The post tanning has been done in two steps; in the first step, small amount of fatliquor has been offered and made into undyed crusts, in the second stage the leathers are dyed and softened well with higher offer of fatliquor. This recipe is adopted in the commercial practice in India to favor the grading process. The control and experimental undyed crust leathers have been compared for their whiteness by reflectance using spectrophotometer. The results of the reflectance measurements of chrome tanned and Gl-Ta tanned crust leathers are shown in Fig 2. From the figure it is clearly seen that the Gl-Ta system results in better whiteness than chrome tanning. The lightness value 'L' for experimental leathers were found to 92%, whereas the same for the control leather was 80%, which is clearly indicative that manufacture of pastel shade garment leather is possible with the experimental Gl-Ta tanning system.

Dyeability of Leathers

In order to study the dyeability of the leathers, in the second stage of post tanning, 8% of acid black dye has been used for both control and experimental leathers. During the dyeing process, the penetration of the dye has been monitored and it was observed that the time required for complete penetration of dye in both processes was about 30 minutes. The intensity and richness of dyeing for experimental crust leather (Gl-Ta tanning) is better compared to control leathers. This could be due to the white base of the experimental tanning system. This provides a scope for reduced offer of dyes for the experimental process to obtain leathers of similar color intensity as that of conventional chrome tanned leathers.

Physical Strength Properties

The tensile, tear and grain burst strength and distension of matched pair leathers tanned using control chromium and Gl-Ta tanning systems are given in Table V. From the table, it is evident that the tensile and grain burst strength of leathers from of Gl-Ta tanning system is high compared to chrome tanned crust leathers. Tear strength of the leathers processed from the two systems is found to be comparable and is around 50 kg/cm. From Table V, it is evident that the physical strength characteristics obtained are all well above the stipulated UNIDO values for garment leather.[18]

Organoleptic Properties

The organoleptic properties of crust leathers processed using chrome and experimental tanning system were compared and same is given in Table VI. The organoleptic properties of chrome and Gl-Ta tanning systems have been found to be similar.

Finishing Characteristics

Matched pair comparison has also been performed to study the finishing characteristics of the developed Gl-Ta tanned crusts with that of the chrome tanned crusts. The wet and dry rub fastness measured for both control and experimental finished leathers process using same composition and quantity of finishing components per unit area are shown in Table VII. From the table, it is observed that the fastness properties of both control and experimental leathers are very much comparable.

Effluent parameters of control and experimental processing

The spent tan liquor analysis from Gl-Ta combination tanning was carried out to evaluate the impact of the same on environmental pollution load. The chemical oxygen demand (COD) and total solids (TS) values for Gl-Ta and control chrome tanning system are shown in Table VIII. It is seen from the table that total solids load is comparable to that of the control chrome tanning system, whereas the COD value is slightly higher. The increase in COD is due to the presence of tara, which is known to increase the COD.

CONCLUSIONS

The tanning system based on the tara and gluteraldehyde combination resulted in garment leathers which were on par with the organoleptic and physical strength properties of chrome tanned leathers. The color of the leathers produced was suitable for making pastel shades. The shrinkage temperature of the leathers made using this combination was above 90°C. Hence, these results suggest that this tara glutaraldehyde tanning system can be used commercially for the manufacture of garment leathers.

Note Identifying Commercial Materials and Chemicals*

Balsyn AL: Aluminium based syntan from Balmer Lawrie & Co. Ltd., India.
Relugan GT 50: Gluterldehyde based retanning agent from BASF, Germany.
Sellasol NG: Neutralizing syntan from TFL, Germany
Relugan RE: Acrylic co-polymer based syntan from BASF, Germany
Basytan DI: Phenol condensate based syntan from BASF, Germany
Tergotan RPF-IN liq: Filling replacement syntan from Clariant Ltd., India
Derminol FS-IN liq: Fish oil substitute from Clariant Ltd., India
Balmol SXE: Synthetic fat liquor from Balmer Lawrie & Co. Ltd., India
Balmol SX-20: Synthetic fat liquor from Balmer Lawrie & Co. Ltd., India
Luwet 40: Wetting agent from Textan Chemicals, India
Tanicor R5-IN p: Resin syntan with polymeric fillers from Clariant Ltd., India
Kroatan 628: Resin based on plastic polymer with long molecular chain from Codyeco s.p.a., Italy.
Kroatan 477: Protein filler syntan from Codyeco s.p.a., Italy.
Softimol licker nappa: Natural sulphited-bisulphited oils together with phosphoesters from Codyeco s.p.a., Italy.
Fospho licker S: Blend of high quality natural oils for waxy touch and light weight from Codyeco s.p.a., Italy.

Lipoderm liquor 2FB: Natural oil based fatliquor from BASF, Germany.
Rodobind 4080: Cationic casein binder from TFL, Germany.
Rodobind EP34: Cationic polyurethane binder from TFL, Germany.
Rodobind 8727: Cationic polyurethane binder from TFL, Germany.
Rodobind R577: Cationic resin binder from TFL, Germany.
Rodowax 619: Cationic wax from TFL, Germany.
ALPA UT: Anionic casein binder from ALPA, Italy.
ALPA 511: Anionic polyamide binder from ALPA, Italy.
ALPA EP19: Anionic polyurethane binder from ALPA, Italy.
Q wax 80: Anionic was emulsion from Quinn India ltd., India.
Fixative BTX: Fixing agent from ALPA, Italy.
GW4: Wax emulsion from Lankro chemicals, UK.
Sensol SW: Wet wax from Earnshaw, UK.

* Editor's note: Mention of trade names or commercial products is solely for the purpose of providing complete information and does not imply an endorsement by the American Leather Chemists Association.

REFERENCES

1. Buljan, J.; Pollution limits for discharge of tannery effluent in water bodies and sewers. *World Leather* **November**, 65, 1996.
2. Leonard, A. and Lauwerys, R.R.; Carcinogenicity and mutagenicity of chromium. *Mut. Res.* **76**, 227, 1980.
3. Flora, S. D., Bagnasco, M., Serra, D. and Zanacchi, P.; Genotoxicity of chromium compounds. *Mut. Res.* **238**, 99, 1990.
4. Balamurugan, K., Rama, R., Ramasami, T. and Sujatha, N.; Chromium(III)-induced apoptosis of lymphocytes: death decision by ROS and Src-family tyrosine kinases. *Free Rad. Biol. Med.* **33**, 1622, 2002.
5. Fathima, N. N., Rao, J. R. and Nair, B. U.; Chromium(VI) formation: Thermal studies on chrome salt and chrome tanned hide powder. *JALCA* **96**, 444, 2001.
6. Covington, A.D.; New tannages for the new millennium. *JALCA* **93**, 168, 1998.
7. Covington, A.D.; Tannages based on aluminium(III) and titanium(IV) complexes. *JALCA* **82**, 1, 1987.
8. Sykes, R.L. and Cater, C.W.; Tannage with aluminium salts. Part 1. Reactions involving simple polyphenolic compounds. *JSLTC* **64**, 29, 1980.
9. Selverangam, R. and Nayudamma, Y.; *Leather Sci.* **11**, 383, 431,481, 1964.
10. Filachione, E.M., Fein, M.L., Harris, E.H. Jr., Luvisi, F.P., Korn, A.H., Windus, W. and Naghski, J.; Tanning with gluteraldehyde. II. Properties of the leathers. *JALCA* 54, 668, 1959.
11. McLaughlin, G.D. and Theis, E.R.; The chemistry of leather manufacture, Reinhold Publishing Corp.: New York, 1945.
12. IUP 2, Sampling, *JSLTC* **84**, 303, 2000.
13. IUP 6, Measurement of tensile strength and percentage elongation, *JSLTC* **84**, 317, 2000.
14. IUP 8, Measurement of tear load - double edge tear, *JSLTC* **84**, 327, 2000.
15. SLP 9 (IUP 9), The Society of Leather Technologists and Chemists, Northampton, 1996.
16. Determination of color fastness to rubbing (Crocking test), Indian Standards, IS 6191 (LF:10), 1971.
17. Clesceri, L.S., Greenberg, A.E. and Trussell, R.R.; Standard methods for the estimation of water and wastewater, 17th edn. American Public Health Association, Washington D.C., 1989.
18. Acceptable quality standards in the leather and footwear industry, United Nations Industrial Development Organization (UNIDO), Vienna, Austria, 1996.