Development of a New Leather Intermediate: Wet-bright with a High Dye Affinity

by
A. Bacardit,[1*] M. González,[1] S. van der Burgh,[2] J. Armengol[2] and L.Ollé[1]
[1]*A_3 Chair in Leather Innovation. Escola d'Enginyeria d'Igualada (EEI). Universitat Politècnica de Catalunya (UPC),*
Avda. Pla de la Massa, 8. 08700 Igualada, Spain
[2]*Kemira ChemSolutions b.v.*
Papesteeg, 91, 4006 WC Tiel, PO Box 60, 4000 AB Tiel, The Netherlands

Abstract

In this work we develop a new tanning process (that we call wet-bright) that produces leather free of chromium, aldehydes, aldehyde precursors and organic solvents. Due to the mineral character of the new system, the leather offers a perfect dyeability and high dye affinity, allowing for very bright colors in all leather applications. The leathers offer a perfect dyeability due to the brilliant whiteness of the wet-bright intermediate. This new system consists of the application of Tanfor T™ system (from Kemira) which is safe for both humans and environment and is not classified as hazardous. In addition, when compared to existing traditional processes, there are economic and environmental advantages resulting from the use of this new system.

Introduction

It is well known that chrome tanning has a strong impact on environment due to the pollution of wastewater and the difficulty to eliminate the solid waste that contains chrome. To reduce the negative environmental impact of the chrome tannage, wet-white tanning is increasingly used.[1-4] However, wet-white leathers mostly consist of aldehyde-based processes, oxazolidine and/or phosphonium compounds.[5-8] This implies using products harmful to human health.

In the present work, we present a new process with the aim of obtaining leather free of chromium, aldehydes, aldehyde precursors and organic solvents.

This new system consists of the application of Tanfor T™ system (from Kemira), which is safe for both humans and environment and is not classified as hazardous. The process is based on a mineral tanning using compounds from aluminum, silicon and natural polycarboxylic acids.

Tanfor T (product launched at the 2012 Tanning Tech in Bologna, Italy) is formulated from environmentally friendly components that are used in water treatment, consumer household products and are partially biodegradable.[9]

Tanfor T™ system is designed as a two-component system:

i) Tanfor T-A is the tanning agent based on aluminum-silicon compounds. It is stable only in a certain pH range. At pH values above their stability range, the mineral salts will precipitate. At low pH, they are fully soluble, giving water clear solutions without signs of turbidity. Just below the maximum pH value of the stability range, a transition range is found where colloidal aggregates are formed. It is the colloidal aggregation state that is relevant for mineral tanning.10

ii) Tanfor T-B is a self-basifying agent, self-buffering basic component of the Tanfor T tanning system, with a very high content of tanning active material.

The wet-bright intermediate that is obtained with Tanfor T is very cationic, which is a good substrate for anionic post tanning formulations.

Material and Methods

Material
The tests were carried out using pickled hides at pH 3.2. Two types of tannages were compared: the chrome tannage (Table I) and the new system using Tanfor T™ (Table II).

The chemicals used in the operations were those normally used in the leather industry.

Methodology
In order to determine the dyeability of the leathers and compare both systems, we carried out the post tanning operations for automotive, upholstery, shoe upper, bovine

*Corresponding author e-mail: anna.bacardit@eei.upc.edu
Manuscript received August 5, 2015, accepted for publication November 26, 2015.

TABLE I
Wet-blue tanning formulation.

(on pickled hides):		
Tanning	**Wet-Blue**	
Water	50%	T = 25ºC
NaCl	5%	rotate - 10' ºBé=8.0 pH = 3.1
Chrome salt 33 ºSchorlenmeyer	2%	rotate – 60'
Chrome salt 66 ºSchorlenmeyer	5.5%	rotate – 2 h
MgO	0.3%	rotate – 6 h Overnight pH = 3.8
Rest (24 h), drain, shave and weigh, neutralize (pH = 5) and retannage, dyeing, fatliquor		

TABLE II
Wet-bright tanning formulation.

(on pickled hides):		
Tanning	**Wet-Blue**	
Water	50%	T = 25ºC
NaCl	5%	rotate - 10' ºBé=7 pH = 3.3
Tanfor T-A	4%	rotate – 3 h
Tanfor T-B	2%	rotate – 2 h
Tanfor T-B	2%	rotate – 2 h Overnight pH = 4.4
Rest (24 h), drain, shave and weigh, neutralize (pH = 5) and retannage, dyeing, fatliquor		

garment and ovine garment (all of them in different colors). The formulations of wet-end followed by each of the articles are shown in Table III, IV, V, VI and VII.

Evaluation
For the purpose of assessing the pollution in wastewaters after obtaining the wet-blue or the wet-bright, the following parameters were analyzed: Conductivity (μ/cm), Suspended solids (mg/L), COD (mg/L), N Kjeldahl (mg/L), Chromium (mg/L).

In order to determine the quality of the leathers and compare both systems, the following official methods were used to this end:

IUP 6 Measurement of tensile strength and percentage elongation (in accordance with EN ISO 3376).

IUP 8 Measurement of tear load (in accordance with EN ISO 3377-2).

IUP 9 Measurement of distension and strength of grain by the ball burst test (in accordance with EN ISO 3379).

IUP 16 Measurement of shrinkage temperature up to 100ºC (in accordance with EN ISO 3380).

With the aim to evaluate the dyeability of the leathers and compare both systems, the color of the leather was analyzed by means of Datacolor, though the CIE 1976 L*a*b* (CIELAB).

The CIE 1976 L*a*b* color space is the most widely used method for measuring and ordering object color. It is routinely employed throughout the world by those controlling the color of textiles, inks, paints, plastics, paper, printed materials, and other objects. It is sometimes referred to as the CIELAB color space.

The 1976 CIELAB color space is a mathematical transformation of the colorimetric system and it can be visualized as a three dimensional space, where every color can be uniquely located. The location of any color in the space is determined by its color coordinates; L*, a*, and b*, where:

L* - is the lightness coordinate.

a* - is the red/green coordinate, with +a* indicating red, and -a*indicating green.

b* - is the yellow/blue coordinate, with +b* indicating yellow, and -b* indicating blue.

The L*, a*, b* color coordinates (of an object) are calculated as follows:

1. The object is measured by a spectrophotometer.
2. A light source (illuminant) is selected.
3. An observer (2° or 10°) is selected.
4. Tristimulus values (X, Y, Z) are computed from the light-object-observer data.
5. L*, a*, and b* are computed from the X, Y, Z data, using the CIE 1976 equations.

TABLE III
Wet-end formulation for automotive.

PHASE	ºC	%	PRODUCT	TIME	REMARKS
WASHING	30	200	Water	10’	
					Drain
NEUTRALISING	30	200	Water		
		0.4	Sodium formiate		
		0.9	Sodium bicarbonate	120’	pH=5.0
RETANNING		10	Condensation product of phenol	30’	
		5	Tara	30’	
		2	Polymeric retanning product	40’	
		10	Condensation product of phenol	30’	
		5	Tara	30’	
DYEING		1	Dye (beige)	240’	
				over night	Through cut
		1	Formic acid (1:10)	60’	pH=3.8
					Drain
WASHING	50	200	Water	15’	
					Drain
FATLIQUORING	50	200	Water		
		4	Lecithin oil		
		8	Sulfited oil	60’	
		1.5	Formic acid (1:10)	30’	pH = 3.2
					Drain
WASHING	40	200	Water	10’	
					Drain

Rest on horse 24h
Setting-out, drying, conditioning, staking and milling

TABLE IV
Wet-end formulation for upholstery.

PHASE	ºC	%	PRODUCT	TIME	REMARKS
WASHING	35	200	Water	10’	
					Drain
NEUTRALISING	35	200	Water		
		2	Sodium formiate	30’	
		0.6	Sodium bicarbonate	20’	
		2	Neutralising agent	120’	pH=5,0
					Drain
RETANNING	35	80	Water		
		3	Polymeric retanning product	60’	
		5	Tara		
		3	Condensation product of phenol		
		2	Dye (brown)	60’	
				Night	Through cut
					Drain
DYEING	50	100	Water		
		0.5	Dye (brown) (1:5)	20’	
		0.8	Formic acid (1:10)	10’	pH= 3,80
		0.5	Dye (brown) (1:5)	20’	Drain
FATLIQUORING	60	100	Water		
		4	Lecithin oil		
		6	Sulfited oil	60’	
		1.5	Formic acid (1:10)	2 x 10’	
				30’	pH= 3,46
					Drain
WASHING	40	200	Water	10’	
					Drain

Rest on horse 24h
Setting-out, drying, conditioning, staking and milling

TABLE V
Wet-end formulation for shoe uppers.

PHASE	ºC	%	PRODUCT	TIME	REMARKS
WASHING	35	200	Water		
		0.4	Acetic acid (1:5)	20’	
					Drain
NEUTRALISING	35	150	Water		
		1.5	Sodium formiate	20’	
		1.0	Sodium bicarbonate		
		2	Neutralising agent	120’	pH=5.2
RETANNING		3	Polymeric retanning product	40’	
		8	Mimosa		
		3	Condensation product of phenol		
		2.5	Dye (brown)	120’	Through cut
					Drain
WASHING	50	200	Water	20’	
					Drain
DYEING	50	100	Water		
		0.7	Dye (brown) (1:5)	20’	
		0.8	Formic acid (1:10)	10’	pH= 3.5
		0.3	Dye (brown) (1:5)	20’	Drain
FATLIQUORING	50	100	Water		
		3	Sulfated oil		
		1.5	Lanonin oil		
		1	Crude oil	60’	
		1.5	Formic acid (1:10)	30’	pH= 3.3
					Drain
WASHING	40	200	Water	10’	
					Drain

Rest on horse 24h
Setting-out, vacuum drying, air drying, conditioning and staking

TABLE VI
Wet-end formulation for bovine garment.

PHASE	ºC	%	PRODUCT	TIME	REMARKS
WASHING	35	200	Water		
		0.1	Acetic acid (1:5)	10’	
					Drain
NEUTRALISING	40	100	Water		
		1.5	Sodium formiate	20’	
		2.3	Sodium ammonium		
		0.5	Sulfited oil	60’	
				Night	pH=6,47
					Drain
RETANNING	40	150	Water		
		3	Polymeric retanning product	60’	
		2	Condensation product of phenol		
		2	Condensation product of phenol with organic nitrogen bases		
		2	Dye (red)	60’	Through cut
					Drain
DYEING	50	100	Water		
		0.5	Dye (red) (1:5)	15’	
		1.6	Formic acid (1:10)	10’	pH= 3,87
		0.3	Dye (red) (1:5)	20’	Drain
FATLIQUORING	55	150	Water		
		5	Phosphatides and synthetic oil		
		5	Sulfated oil		
		2.5	Sulfited oil	60’	
		1.5	Gambier	20’	
		1	Formic acid (1:10)	15’	pH= 3,42
					Drain
WASHING	40	200	Water	10’	
					Drain

Rest on horse 24h
Setting-out, soft vacuum drying, air drying, conditioning and staking

TABLE VII
Wet-end formulation for ovine garment.

PHASE	ºC	%	PRODUCT	TIME	REMARKS
WASHING	35	200	Water		
		0.5	Surfactant	20’	
					Drain
RETANNING	35	200	Water		
		4	Chromium-containing condensation product of phenolic sulphonic acids	60’	
		1.5	Sodium formiate	60’	pH= 4.2
					Drain
NEUTRALISING	35	150	Water		
		1	Sodium formiate	20’	
		1.7	Sodium bicarbonate	2 x 15’	
				60’	pH= 6.2
					Drain
DYEING	35	70	Water		
		2	Dispersing agent and levelling color		
		3	Dye (blue)	60’	Through cut
FATLIQUORING	55	130	Water		
		4	Sulfited oil		
		4	Phosphatides and synthetic oil		
		1	Lanolin oil	60’	
		3	Polymeric retanning product	45’	
		2	Formic acid (1:10)	2 x 15’	
				30’	pH= 3.7
					Drain
WASHING	40	200	Water	10’	
					Drain

Rest on horse 24h
Setting-out, drying, conditioning, staking, wheeling, milling and straining

A color can also be described and located in CIELAB color space using an alternate method, that of specifying its L*, C*, and h* coordinates. In this method, the L* coordinate is the same as in L*a*b*, while the C* and h* coordinates are computed from the a* and b* coordinates. The same color is still in the same location in the color space, but there are two different ways to describe its position (L*a*b* or L*C*h*).

The L*C*h* color space is also three dimensional, but the color is located using cylindrical coordinates, as follows:

L* - the lightness coordinate, same as in L*a*b*.

C* - the chroma coordinate, the distance from the lightness axis.

h* - the hue angle, expressed in degrees, with 0° being a location on the +a* axis, then continuing to 90° for the +b* axis, 180° for -a*, 270° for -b*, and back to 360° = 0°.

In addition, we can calculate the color differences between different samples. The method consists in calculate the distance between the color locations. This distance can be expressed as delta E CIE L*a*b*, where:

$\Delta E^* = (\Delta L^*2 + \Delta a^*2 + \Delta b^*2)^{1/2}$.

ΔL^* being the liqhtness difference.

Δa^* being the red/green difference.

Δb^* being the yellow/blue difference.

For those preferring to express differences in chroma and hue terminology, instead of da* and db*, the following terms are utilized:

$\Delta E^* = (\Delta L^*2 + \Delta C^*2 + \Delta H^*2)^{1/2}$

ΔC^* being the chroma difference.

Δh^* being the hue angle difference.

ΔH^* being the metric hue difference.

The ΔE^* and ΔL^* differences are the same, whether using L*a*b* or L*C*h*.

The CIELAB system is often used to facilitate the quality control of colored products. In these cases, the color of the production sample is located in CIELAB space, and compared to the color standard for production.

In our case, the standard used in each test is the wet-blue leather.

RESULTS AND DISCUSSION

The aim of the first stage of this study is to assess whether the leathers processed with Tanfor T™ system (i.e. wet-bright) present advantages over the chrome-tanned leathers.

As can be seen in Table VIII, lower values both in tear load (IUP 8) and in shrinkage temperature (IUP 16) are obtained as compared with those obtained in wet-blue leathers. Wet-bright leathers are more comparable to wet-white using aldehydes. The great advantage of using Tanfor T™ is that wet-bright leathers do not contain chromium. Table IX shows the comparison of pollution in wastewaters between the wet-blue and wet-bright.

Chrome tanning is one of the most polluting processes in leather industry due to the presence of chromium in the resulting wastewaters. Thus, wet-bright presents again an advantage respect wet-blue. Specifically, wet-bright reduces by 60% in COD respect wet-blue. As compared with wet-blue, wet-bright reduces by 61% in suspended solids and reduces by 65% in nitrogen. And most important, wastewater does not contain chromium.

TABLE VIII
Comparison of physical tests.

TEST	WET-BLUE	WET-BRIGHT
Tensile strength (N)	-269.3 ± 1.5	-256.6 ± 1.8
Tear load (N/mm)	-102.7 ± 1.1	-64.8 ± 0.8
Strength of grain (kg)	-31.7 ± 1.0	-28.3 ± 0.9
Shrinkage temperature (ºC)	106.5 ± 0.5	-83 ± 0.5

TABLE IX
Comparison of pollution in wastewaters.

TEST	WET-BLUE	WET-BRIGHT
Conductivity (µS /cm)	-86010 ± 44	-101511 ± 55
Suspended solids (mg/L)	-1152 ± 20	-467 ± 18
COD (mg/L)	-9350 ± 40	-3790 ± 30
N – Kjeldahl (mg/L)	-467 ± 5	-168 ± 5
Chromium (mg/L)	-3221.2 ± 3.4	No detectable

Once the advantages of the new system have been established, we study the dyeability of the new system.

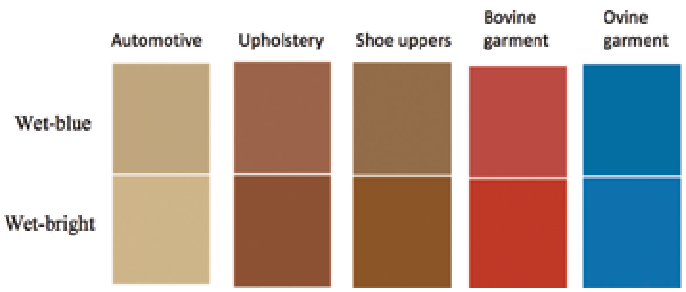
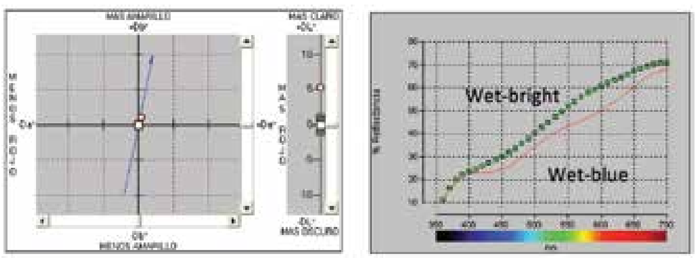


Figure 1. Comparison of the colours obtained.

Figure 1 shows the differences in the colors obtained when using wet-blue or wet-bright leathers by means of the Datacolor. As can be seen, wet-bright leathers offer- a higher dye affinity, obtaining more intense and more brilliant colors.

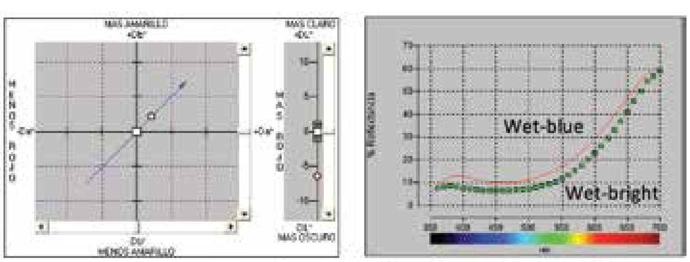
Figure 2, 3, 4, 5 and 6 show the graph with L,a,b coordinates for each article (in the left), the percentage of reflectance for each sample (in the right), as well as a table with all the calculated coordinates and color difference.



Illum./Obs.	DL*	Da*	Db*	DC*	DH*	Cielab DE*	DE CMC	DE*ad
D65 10 Deg	5.34	0.49	1.01	1.09	-0.28	5.45	2.18	4.23
A 10 Deg	5.44	-0.04	1.09	1.01	0.41	5.55	2.19	4.47
F11 10 Deg	5.49	0.44	1.27	1.33	-0.20	5.65	2.23	4.63

Figure 2. Datacolor analysis for Automotive.

As can be seen in Figure 2, the wet-bright leathers show clearer color; redder and more saturated. The difference in the color is 81.82% of intensity respect to wet-blue leathers. The central point in the left graph corresponds to wet-blue leathers.

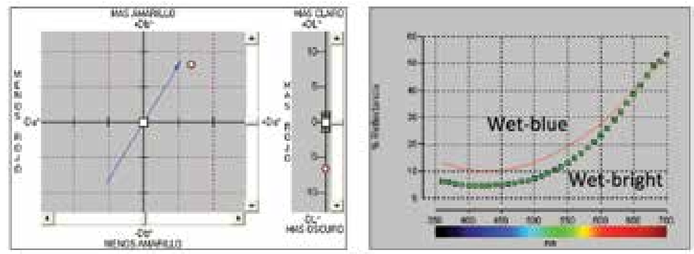


Illum./Obs.	DL*	Da*	Db*	DC*	DH*	Cielab DE*	DE CMC	DE*ad
D65 10 Deg	-6.41	2.20	2.18	3.10	-0.02	7.12	3.27	2.41
A 10 Deg	-6.07	2.30	2.65	3.51	0.00	7.01	3.07	2.74
F11 10 Deg	-6.38	1.73	2.30	2.87	0.07	7.00	3.16	2.62

Figure 3. Datacolor analysis for Upholstery.

As can be seen in Figure 3, the wet-bright leathers show darker color; redder and more saturated. The difference in the color is 168.45% of intensity respect to wet-blue leathers.

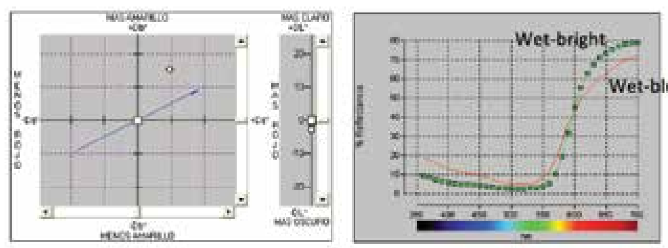
As can be seen in Figure 4, the wet-bright leathers show darker color; redder and more saturated. The difference in the color is 236.94% of intensity respect to wet-blue leathers.



Illum./Obs.	DL*	Da*	Db*	DC*	DH*	Cielab DE*	DE CMC	DE*ad
D65 10 Deg	-6.63	6.84	8.13	10.54	-1.34	12.52	6.54	10.58
A 10 Deg	-5.54	6.73	9.80	11.89	-0.27	13.12	6.18	12.00
F11 10 Deg	-6.20	5.88	8.92	10.67	-1.24	12.40	6.34	11.47

Figure 4. Datacolor analysis for Shoe upper.

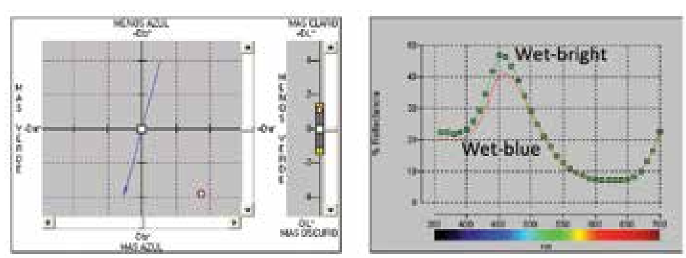
As can be seen in Figure 5, the wet-bright leathers show darker color; more yellow and more saturation. The difference in the color is 191.69% of intensity respect to wet-blue leathers



Illum./Obs.	DL*	Da*	Db*	DC*	DH*	Cielab DE*	DE CMC	DE*ad
D65 10 Deg	-2.82	8.67	15.28	16.09	8.21	18.28	8.37	13.81
A 10 Deg	-1.18	8.67	17.80	19.14	6.39	20.21	8.50	15.77
F11 10 Deg	-1.11	9.09	18.67	18.29	8.82	20.71	8.77	16.32

Figure 5. Datacolor analysis for Bovine garment.

As can be seen in Figure 6, the wet-bright leathers show clearer color; redder and more saturated. The difference in the color is 91.31% of intensity respect to wet-blue leathers.



Illum./Obs.	DL*	Da*	Db*	DC*	DH*	Cielab DE*	DE CMC	DE*ad
D65 10 Deg	1.11	3.51	-3.82	3.92	4.22	5.30	3.29	5.65
A 10 Deg	1.02	1.49	-3.83	2.78	2.77	4.05	2.04	4.26
F11 10 Deg	1.09	2.60	-4.10	3.88	3.08	4.92	2.63	5.24

Figure 6. Datacolor analysis for Ovine garment.

The cationic character and even distribution of aluminum-silicon compounds in the wet-bright intermediate, together with the whiteness, provide an excellent substrate for colors. If we observe all figures (2-6), compared to wet-blue, the dye uptake is higher in 3 of 5 formulas, and the colors are more sparkling due to the bright white base color obtained using Tanfor T™.

Conclusions

The leathers obtained with this process are free of chromium, aldehydes precursors and organic solvents. In addition, the new system is an environmentally friendly process due to the reduction by 60% in COD, reduction by 61% in suspended solids, and reduction by 65% in nitrogen compared with chromium tannage.

The new tanning process based on aluminum-silicon compounds produces perfectly white leathers. The whiteness and strong cationic character of the base allows for very bright colors. Compared to wet-blue, the dye uptake is very high and the colors are more sparkling due to the bright white base color obtained using Tanfor T™.

References

1. Thanikaivelan, P., Rao, J.R., Nair, B.U., Ramasami, T.; Underlying principles in chrome tanning: Part II. Underpinning mechanism in pickle-less tanning. *JALCA* **99**, 83, 2004.
2. Saravanabhavan, S., Aravindhan, R., Thanilaivelan, P., Chandrasekaran, B., Rao, J.R., Nair, B.U.; An integrated eco-friendly tanning method for the manufacture of upper leather from goatskins. *JSLTC* **87**, 149, 2003.
3. Muralidharan, M., Sundar, V.J., Sundara Rao, V.S., Ramasami, T.; Two stage tanning – A new approach for chrome management. *JALCA* **96**, 61, 2001.
4. Morera, J.M., Bacardit, A., Ollé, L., Bartolí, E., Borràs, M.D.; Minimization of the environmental impact of chrome tanning: a new process with high chrome exhaustion. *Chemophere* **69**, 1728-1733, 2007.
5. Wolf, G., Breth, M., Carle, J., *et al*.; New developments in wet-white tanning technology. *JALCA* **96**, 111, 2001.
6. Jayakumar, G. D., Santana Bala, L., Kanth, S.V., Chandrasekaran, B., Rao, J.R., Nair, B.U.; Combination Tanning System Based on Dialdehyde Alginic Acid: An Ecofriendly Organic Approach. *JALCA* **106**, 4, 113-120, 2011.
7. Taylor, M.M., Lee, J., Bumanlag, E., Hernandez Balada, E., Brown, E.M.; Treatments to Enhance Properties of Chrome-free (Wet white) Leather. *JALCA* **106**, 2, 35-43, 2011.
8. Ollé, L., Jorba, M., Font, J., Shendrik, A., Bacardit, A.; Biodegradation of wet-white leather. *JSLTC* **95**, 116, 2011.
9. van der Burgh, S.; New mineral tanning system. *Leather International*, 22-24. www.leathermag.com, 2012.
10. Bacardit, A., van der Burgh, S., Armengol, J., Ollé, L.; Evaluation of a new environment friendly tanning process. *Journal of Cleaner Production* **65**, 568-573, 2014.