Study of the Effect of Temperature, Relative Humidity and UV Radiation on Chrome-tanned Leather Ageing

by

Anna Bacardit*, Montse Jorba[1], Joaquim Font, and Luís Ollé
Igualada Engineering School (EEI). UPC.
Plaça del Rei, 15. 08700-Igualada (Spain)

[1]*Asociación de Investigación de las Industrias de Curtidos y Anexas (AIICA).*
Avda. Pla de la Massa s/n, 08700 Igualada, Spain

Abstract

Since leather is strongly affected by three main environmental parameters: temperature, relative humidity and UV radiation, this piece of research focuses on the effect that these three factors have on chrome-tanned leather ageing. Chrome tanned leathers were exposed to weathering effects in a climatic chamber in order to identify the most important variables affecting this weathering process and also to check for any possible interactions. Both a multilevel centralized factorial experimental design and an analysis of variance (ANOVA) were used as statistical tools for estimating the effects of the parameters.

Resumen

Ya que el cuero es fuertemente afectado por tres principales parámetros ambientales: temperatura, humedad relativa, y radiación UV [Ultra-Violeta], esta porción investigativa se enfoca en los efectos que estos tres factores tienen sobre el envejecimiento del cuero curtido al cromo. Cueros curtidos al cromo fueron expuestos a los efectos climáticos en una cámara climática con el fin de identificar las variables más importantes que afectan a este proceso climático y así también investigar cualesquier interacciones posibles. Ambos, un diseño experimental factorial de múltiples niveles con un análisis de varianza (ANOVA) fueron utilizados como herramientas estadísticas para estimar los efectos de los parámetros.

*Corresponding author e-mail: annab@euetii.upc.edu; Tel.: +34-93-803-5300;
Fax: +34-93-803-1589 Manuscript received November 3, 2011, accepted for publication January 7, 2012

Introduction

Automotive upholstery leather is a material that can be used in different environments. Therefore, this type of leather can be subjected to aggressive environmental conditions that will cause its premature ageing.[1-13] Despite the fact that different automobile brands have described their own quality standards and requirements to be met and carried out strict ageing tests, it is not very easy to conduct lab simulations due to the wide variety of causes that may lead to premature ageing. Most research into weathering tests methods has been conducted by plastics, textile, and coatings industries. Sunlight, temperature, and moisture often play critical roles in degradation of these materials in end-use. Consequently, researchers include these factors in the development of weathering test methods.[14-18]

In addition, leather is strongly affected by these three main environmental parameters: temperature, relative humidity, and UV radiation.[19-30] An earlier piece of work studied the effect of the temperature, relative humidity, and UV radiation on wet-white leather. According to the study, relative humidity was the factor with the highest impact on most of the properties analyzed. Since it played a key role in weathering, it consequently did so in wet-white leather ageing.[31] However, as it has been reported in other studies, chrome-tanned leather and wet-white leather show a different behavior to the parameters which affect the weathering process.[32-35] In the present work, the leathers with a chrome tannage were exposed to the three main environmental parameters, i.e., temperature, relative humidity and UV radiation. A climatic chamber was used in order to identify the most important variables affecting the chrome-tanned leather ageing and to compare the ageing process in both types of tannage.

Experimental

Material

the tests were carried out using Spanish chrome tanned cattle hides shaved at 1.2-1.3 mm. The hides were neutralized at pH = 5.5 and retanned using synthetic agents and resins. The hides were then dyed using black dye and fatliquored using oxi-sulphited marine oil, soya lecithin, and sulphonated beef tallow. Finally, the hides were dried (vacuum-air) and milled. The finishing consists in applying a base coat using pigment, oil, wax, acrylic resin, and two types of polyurethane (3-4 dry grams of base coat per square foot of leather in total) by means of air spraying and pressing at 80ºC / 80 bar / 1''. After that, the leathers were top coated using two types of polyurethane and crosslinker (0.5 dry grams of top coat per square foot of leather in total) by means of air spraying and pressing at 80ºC / 80 bar / 1''. Finally, the leathers were milled and toggled.

Methodology

During a period of 7 days, the leathers were exposed to weathering effects using a climatic chamber 1000L / Dycometal model CCK 0/1000 with the aim to both identify the most important variables affecting this weathering process and to check for any possible interactions.

A multilevel centralized factorial experimental design and an analysis of variance (ANOVA) were employed as statistical tools for estimating the effects of the parameters. An experimental design with 3 variables and 2 levels (2^3) was chosen in order to carry out the experiment. The variables to study were: temperature, relative humidity, and UV radiation. Table I shows the twelve experiments required for this experiment. High and low settings for each input variable were selected according to Table I. The experimental results were obtained as the average value of three different measurements.

TABLE I
Experimental Design

TEST	X1	X2	X3	T	Hr	UV*
1	-1	-1	-1	0	0	0
2	1	-1	-1	70	0	0
3	-1	1	-1	0	95	0
4	1	1	-1	70	95	0
5	-1	-1	1	0	0	4
6	1	-1	1	70	0	4
7	-1	1	1	0	95	4
8	1	1	1	70	95	4
9	0	0	0	35	47.5	2
10	0	0	0	35	47.5	2
11	0	0	0	35	47.5	2
12	0	0	0	35	47.5	2

*The leathers were exposed to UV radiation for 4 days (220 MJ/m^2 in total) and for 2 days (110 MJ/m^2 in total) using a Suntest XLS+ Atlas equipped with a xenon lamp and window glass filter.

Evaluation

In order to study the effect of temperature, relative humidity, and UV radiation on leather ageing, we carried out the following tests:

IUP 8. Measurement of tear load.

IUP 9. Measurement of distension and strength of grain by the ball burst test.

IUP 16. Measurement of shrinkage temperature.

IUP 36. Measurement of leather softness.

IUF 450. Color fastness of leather to dry and wet rubbing (1000 and 50 rubs).

IUC 4. Determination of matter soluble in dichloromethane.

IUC 6. Determination of water soluble matter, water soluble inorganic matter, and water soluble organic matter.

Color of the leathers was measured using a spectrophotometer (Datacolor International, Spectraflash SF300).

The infrared spectra of leather surface were recorded using an Infrared Spectrometer with Attenuated Total Reflectance (Perkin-Elmer Spectrum One FTIR with UATR accessory) and Spectrum v5.0.1. software for the visualization of changes among spectra.

To examine the changes in fibrous structure of the leather samples, we used the scanning electron microscopy JEOL JSM 6400.

Results and Discussion

Effect of the weathering variables on physical and fastness properties of the leather

Table II presents the results obtained for each of the properties analyzed.

The statistical analysis of the results obtained was carried out using the Statgraphics Plus Program. The results of the main effects for each of the properties studied are graphed in Figure 1, showing the effect of relative humidity, temperature, and UV radiation factors analyzed in this experiment. The coefficients of the main effects describe the individual influence corresponding to each factor as well as their interactions on the measured properties. The statistically valid regression coefficients of the polynomial models fitted to the experimental data are the following:

a. Shrinkage Temperature = 107.8 – 0.5*T + 1.0*Hr – 1.5*UV + 0.25*T*Hr – 0.75*T*UV – 1.75*Hr*UV

b. Tear load = 126.9 – 10.25*T – 15.85*Hr – 19.15*UV + 9.45*T*Hr + 8.7*T*UV + 12.3*Hr*UV

c. Grain distension = 16.9 – 0.25*T + 0.22*Hr + 0.12*UV – 0.27*T*Hr + 0.07*T*UV + 0.35*Hr*UV

d. Dry rubbing = 4.2 – 0.2*T – 0.3*Hr – 0.6*UV – 0.06*T*Hr – 0.06*T*UV – 0.19*Hr*UV

e. No factor was found significant in wet rubbing.

f. Color loss = 82.5 – 0.49*T – 0.5*Hr – 1.1*UV – 0.1*T*Hr + 0.19*T*UV + 0.42*Hr*UV

g. Softness loss = 2.6 – 0.04*T + 0.01*Hr + 0.1625*UV – 0.1*T*Hr -0.01*T*UV – 0.01*Hr*UV

As can be seen in the Pareto charts shown in Figure 1, UV radiation has, by far, the largest effect on all properties studied except for the grain distension. Relative humidity also

TABLE II
Effect of the weathering variables on physical and fastness properties

TEST	Shrinkage T ºC	Tear load N/mm	Grain dist. mm	Dry rub	Wet rub	Color loss*	Softness loss mm
1	108	198.8	16.7	5	1	85,57	2,3
2	106	138.8	17.0	5	1	84,15	2,5
3	114	120.4	17.4	5	1	83,62	2,6
4	111	104.6	15.8	4-5	1	82,31	2,3
5	108	115.3	16.5	4-5	1	81,80	2,7
6	107	96.5	16.3	4	1	81,67	2,8
7	108	92.5	17.8	3-4	1	82,04	2,9
8	104	105.1	17.3	3	1	81,00	2,6
9	107	137.7	17.0	4	1	82,20	2,6
10	107	137.5	16.9	4	1	82,00	2,5
11	107	137.1	17.1	4	1	82,15	2,6
12	107	138.0	17.0	4	1	81,90	2,7

*The results are expressed as percentage of color variation with regard to the white test (i.e., leather sample without weathering exposure)

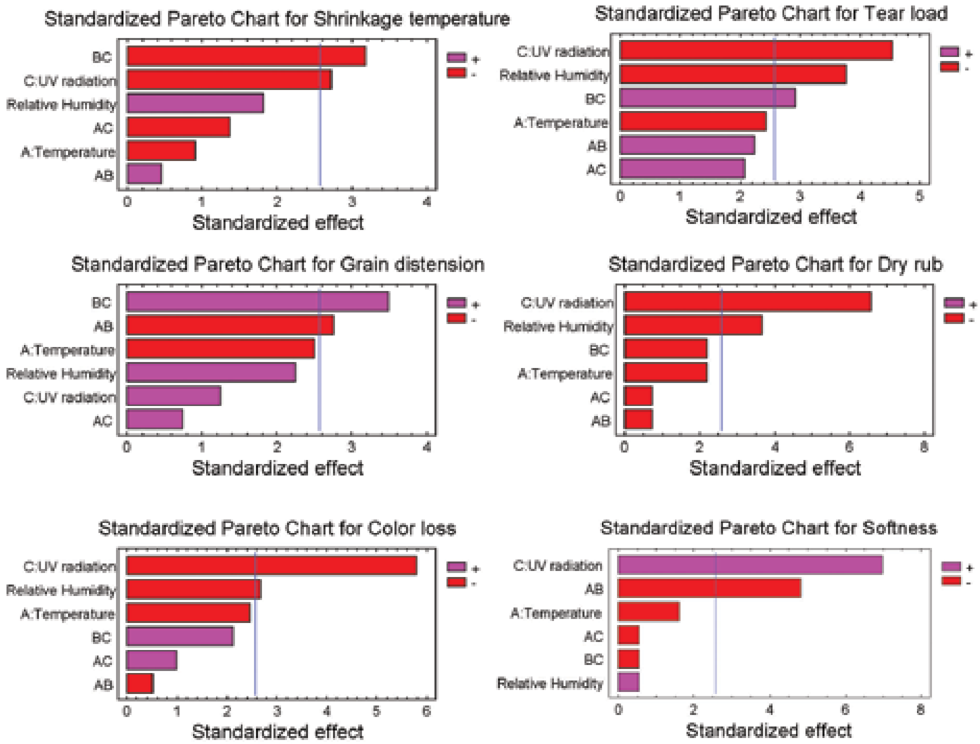

Figure 1. Statistical analysis of the effect of the weathering variables on physical and fastness properties

shows a significant effect on tear load, dry rub and color loss. The analysis also indicates the possibility of a two-way interaction between UV radiation and relative humidity. This effect appears in shrinkage temperature, tear load and grain distension.

As reported in previous studies,[31-35] wet-white leather and chrome-tanned leather show a different behavior to leather ageing. Relative humidity was the factor in wet-white leather with the highest impact on most of the physical and fastness properties analysed, whereas in chrome-tanned leather it was UV radiation. This may be due to the fact that the substances that act as tans and retans in wet-white leathers are not much rich in chromophore groups likely to absorb energy in the form of light. However, humidity accelerates the hydrolysis processes involving the decomposition of these substances (i.e. tans and retans in wet-white leathers). This is contrary to what occurs with chrome complexes. Apart from visible light absorption, chrome complexes have high UV light absorption.

Effect of the weathering variables in the modification of the leather composition

Table III shows the results of the chemical analysis of the leather samples.

For each of the studied properties, the standardized Pareto chart is shown in Figure 2. In addition, the following mathematic models for each of the properties analyzed were established:

h. IR = 0.09 + 0.016*T + 0.01* Hr + 0.03*UV + 0.02*T* Hr -0.015*T*UV – 0.008* Hr*UV

i. Water soluble inorganics = 0.5 – 0.025*T – 0.075*Hr + 0.025*UV – 0.05*T*Hr

j. No factor was found significant in water soluble organics

k. Fats = 9.2 – 0.2*T – 0.3*Hr – 0.8*UV + 0.01*T*Hr + 0.01*T*UV – 0.04*Hr*UV

As can be seen in the Pareto charts shown in Figure 2, UV radiation has again the largest effect on IR and on matter soluble in dichloromethane. Temperature also shows a significant effect on IR. The analysis also indicates the possibility of a two-way interaction between temperature and relative humidity, and between temperature and UV radiation. The results obtained with the IR spectra are consistent with those observed in matter soluble in dichloromethane, which are responsible for a significant portion of the absorption bands of the spectra. The results are also consistent with those observed in the loss of leather softness since a further tightening of the skin implies a loss of signal in the spectra obtained through the ATR technique used.

The amount of soluble organic matter content in the leathers used is very low. It has also been observed that the processes of ageing have not lead to the hydrolysis of the resin and synthetic retanning agents that the leather contains. This result could have been different if the formula had considered retanning agents with less fastness to environmental effects.

The results show that water soluble inorganic matter and matter soluble in dichloromethane are affected by weathering exposure. This conforms that weathering exposure causes radical reactions in such a way that some of the bonds between collagen and tanning agents and/or fatliquors break. Interestingly, relative humidity and an interaction between temperature and relative humidity were found significant in water soluble inorganic matter. On the other hand, matter soluble in dichloromethane is affected by UV radiation. It is known how nonsaturated oils can form free radicals when exposed to light.[7,10-13] In the fattening formulation, a fish oil, among others, has been used. Despite being a product that has undergone a treatment of stabilization (it is oxi-sulphited), it contains alkene groups. Therefore, it makes sense that such component is the most sensitive to the effect of light. In the case of water soluble inorganic matter relative humidity act as a chemical reagent in hydrolytic weathering reactions.

TABLE III
Effect of the weathering variables on modification of the leather composition

TEST	IR*	Water soluble organics %	Water soluble inorganics %	Fats %
1	0.0290	0.1	0.5	10.7
2	0.0651	0.1	0.6	10.4
3	0.0400	0.1	0.5	10.3
4	0.1306	0	0.3	9.6
5	0.1581	0.1	0.6	9.4
6	0.0916	0	0.6	8.7
7	0.0943	0.1	0.5	8.4
8	0.1680	0.1	0.4	8.2
9	0.0871	0.1	0.5	8.8
10	0.0871	0.1	0.5	8.7
11	0.0871	0.1	0.5	8.9
12	0.0871	0.1	0.5	8.8

**Absorbance of IR spectrum* was calculated as the sum of the corrected absorbance at 2923 cm^{-1}, 1730 cm^{-1}, and 798 cm^{-1} of the infrared spectrum recorded by ATR for each sample (*Absorbance of IR spectrum* = $Abs_{2923\,cm^{-1}} + Abs_{1730\,cm^{-1}} + Abs_{798\,cm^{-1}}$)

Changes in fibrous structure

Figure 3 shows the cross-section of leather samples no.1, no.8 and no.9 to examine the changes in fibrous structure due to the effect of the temperature, relative humidity, and UV radiation.

Sample no.1 was exposed to low settings for each factor (i.e., 0ºC, 0% Hr, and without UV radiation).

Sample no.9 was exposed to medium settings for each factor (i.e., 35ºC, 47,5 % Hr, and 110 MJ/m^2).

Sample no.8 was exposed to high settings for each factor (i.e., 70ºC, 95% Hr, and 220 MJ/m^2).

A slight loss in compactness can be observed in the fibers possibly as a result of the hydrolysis of collagen, since the protein chain of collagen has been exposed to high levels of humidity. However, this slight loss of compactness is almost negligible compared with that obtained in the wet-white leather (see Study of the effect of temperature, relative humidity and UV radiation on wet-white leather ageing, JALCA, Vol. 105, 2010, 334-341).

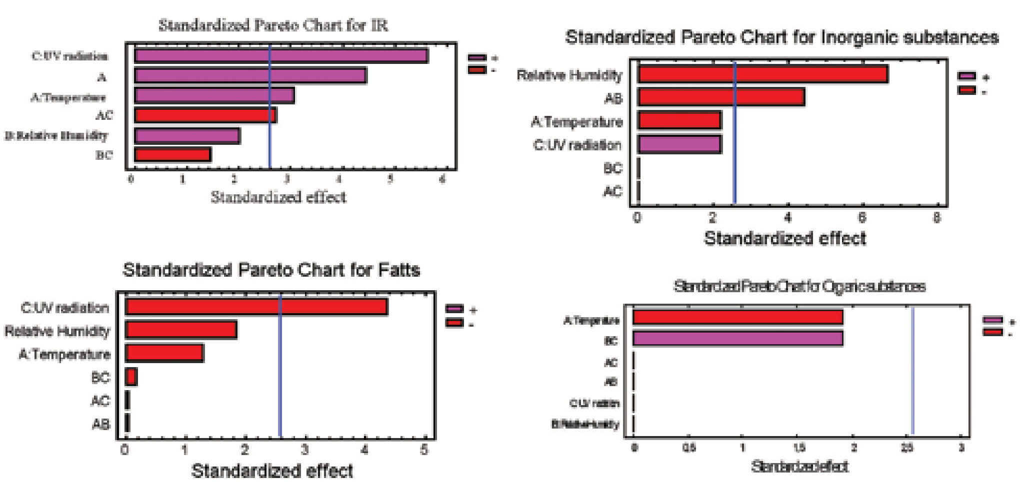

Figure 2. Statistical analysis of the effect of the weathering variables on modification of the leather composition

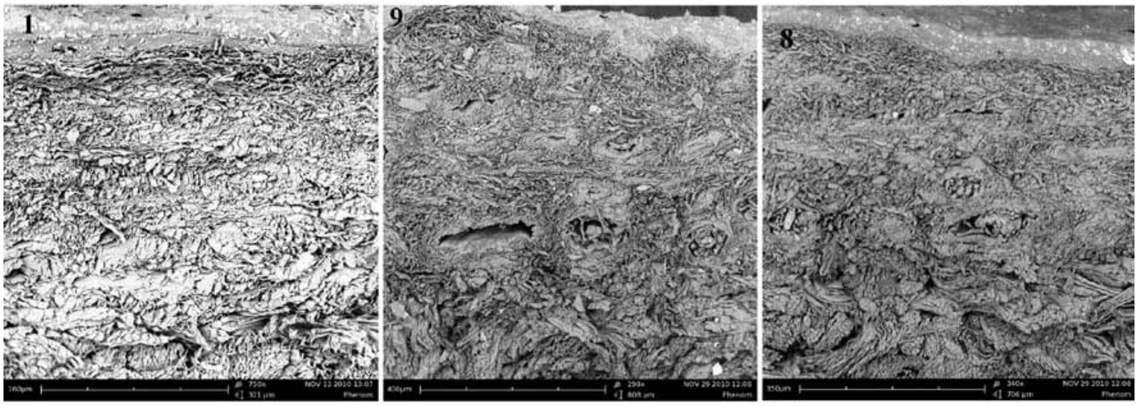

Figure 3. Micrograph (SEM) of cross-section of leather samples no.1, 9, and 8

Conclusions

The aim of this study was to examine the effect of the temperature, relative humidity, and UV radiation on chrome-tanned leather ageing. UV radiation was the factor with the highest impact on most of the properties analyzed. Therefore, it plays a key role in weathering and consequently in leather ageing. Chrome-tanned leather and wet-white leather show a different ageing behavior. Whereas chrome-tanned leathers are strongly affected by UV radiation, wet-white leathers are strongly affected by relative humidity.

No correlation has been found between ageing caused by natural weathering and that caused under controlled conditions in the laboratory.

References

1. Nungesser, E.; Kar, A.; Yang, D.; Hageman, B.; Novel Acrylic/Silica-Free Matting Technology for Furniture Leather Upholstery Topcoat Finishes, in Proceedings of the XXIX International Union of Leather Technologists and Chemists Societies Congress, Washington, 2007
2. Hörner, K.D.; Dreiβgacker, G.; Innovative finishes for automotive leather, *Leather International* **10**, 29, 2004
3. Simpson, P.; Hörner, K.D.; Dreiβgacker, G.; Salgado, J.; Carod, A.; Innovation for the upgrading of the automotive leathers. *World Leather* **7**, 31, 2005
4. Nungesser, E.; Hoefler, J.; Enhanced acrylic technology for automotive topcoat finishes, *JALCA* **100**, 54, 2005
5. Policky, F.S.; The challenge of European automotive upholstery finishes, *JSLTC* **74**, 99, 1989
6. Kaussen, M.; Update on the production of automotive leathers, *JALCA* **84**, 353, 1989
7. Püntener, A.; The influence of fatliquors on the lightfastness of dyed leather, *JALCA* **91**, 126, 1996
8. Sammarco, U.; Formation of Cr (VI) in leather and possibility of elimination, *Cuio, Pelli, Materie Concianti,* **74**, 83, 1998
9. Font, J.; Cuadros, R.M.; Reyes, M.R.; Costa-López, J.; Marsal, A.; Influence of various factors on chromium (VI) formation by photo-ageing, *JSLTC* **83**, 300, 1999
10. Segura, R.; Palma, J.J.; Izquierdo, F.; Anti-aging in leather, in Proceedings of the 49º congreso AQEIC, Palma de Mallorca, España, 2000
11. de Volder, N.; Hallmanns, M.; Levy, J.; Annoying energy. II. Solar heating of dark leather, in Proceedings of the XXIX International Union of Leather Technologists and Chemists Societies Congress, Washington, 2007
12. Palop, R.; Parareda, J.; Ballús, O.; Gomera, A.; Influence of fatliquoring products in leather aging and formation of Chromium VI. Part I, in Proceedings of the 56º Congreso AQEIC, Cartagena, España, 2007
13. Palop, R.; Parareda, J.; Ballús, O.; Gomera, A.; Influence of fatliquoring products in leather aging and formation of Chromium VI. Part II, in Proceedings of the 56º Congreso AQEIC, Cartagena, España, 2007
14. Deflorian, F.; Rossi, S.; Fedrizzi, L.; Zanella, C.; Comparison of organic coating accelerated tests and natural weathering considering meteorological data, *Prog. Org. Coat.,* **59**, 244, 2007
15. Malshe, V.C.; Waghoo, G.; Weathering study of epoxy paints, *Prog. Org. Coat.,* **51**, 267, 2004
16. Croll, S.G.; Hinderliter, B.R.; Liu, S.; Statistical approaches of predicting weathering degradation and service life, *Prog. Org. Coat.*, **55**, 75, 2006
17. Irigoyen, M.; Aragon, E.; Perrin, F.X.; Vernet, J.L.; Effect of UV ageing on electrochemical behavior of an anticorrosion paint, *Prog. Org. Coat.*, **59**, 259, 2007
18. Hardcastle III, H.K.; Characterizing the effect of weathering variables using accelerated fractional factorial experiments. Natural test methods and artificial ageing of polymers; Thomas Reichert, ed. Pinsfal, Germany. Gesellschaft fur Umweltsimulation. 2004
19. Kite, M.; Thomson, R.; Conservation of leather and related materials; Elsevier, Oxford. 2000
20. Bickley, J.C.; Vegetable tannins. In Leather, its composition and changes with time; C. Calnan and B. Haines, eds. Northampton: The Leather Conservation Center. 1991

21. Bowes, J.H.; Raistrick, A.S.; The action of heat and moisture on leather. V. Chemical changes in collagen and tanned collagen, *JSLTC* **29**, 201, 1964
22. Calnan, C.N.; Ageing of vegetable tanned leather in response to variations in climatic conditions. In Leather, its composition and changes with time; C. Calnan and B. Haines, eds. Northampton: The Leather Conservation Center. 1991
23. Chahine, C.; Acidic deterioration of vegetable tanned leather. In Leather, its composition and changes with time; C. Calnan and B. Haines, eds. Northampton: The Leather Conservation Center. 1991
24. Florian, M.-L.E.; A holistic interpretation of the deterioration of vegetable tanned leather; *Leather Conservation News* **2**, 1, 1985
25. Haines, B.; Natural ageing of leather in libraries. In Leather, its composition and changes with time; C. Calnan and B. Haines, eds. Northampton: The Leather Conservation Centre. 1991
26. Haines, B.; Deterioration under accelerated acidic ageing conditions. In Leather, its composition and changes with time; C. Calnan and B. Haines, eds. Northampton: The Leather Conservation Centre. 1991
27. Haines, B.; The structure of collagen. In Leather, its composition and changes with time; C. Calnan and B. Haines, eds. Northampton: The Leather Conservation Centre. 1991
28. Larsen, R.; Experiments and observations in the study of environmental impact on historical vegetable tanned leathers; *Thermochimica Acta* **365**, 85, 2000
29. Larsen, R.; Vest, M.; Nielsen, K.; Determination of hydrothermal stability (Shrinkage Temperature) of historical leather by the Micro Hot Table Technique, *JSLTC* **77**, 151, 1993
30. Thomson, R.; Conserving historical leathers: Saving our past for the future, *JALCA* **97**, 307, 2002
31. Bacardit, A.; Cobos, M.; Font, J.; Jorge, J. ; Ollé, L. ; Study of the effect of temperature, relative humidity and UV radiation on wet-white leather ageing, *JALCA* **105**, 334, 2010.
32. Font, J.; Espejo, J.; Cuadros, S.; Reyes, M.R.; Bacardit, A.; Butí, S.; Comparison of IUP 16 and Microscopic Hot Table Methods for Shrinkage Temperature Determination, *JSLTC* **94**, 59, 2010.
33. Bacardit, A.; Jorba, M.; Font, J.; Shendrik, A.; Ollé, L.; Biodegradation of leather tanned with inorganic salts, *JSLTC* **95**, 2, 2011
34. Ollé, L.; Jorba, M.; Font, J.; Shendrik, A.; Bacardit, A.; Biodegradation of wet-white leather, *JSLTC* **95,** 3, 2011
35. Ollé, L.; Cobos, M.; Font, J.; Bacardit, A.; Comparison of leather aging due to tropical environment exposure and natural weathering, *JSLTC* **95**, 2, 2011

WET-END FORMULATION
(on wet-blue weight)

Neutralization	**100%**	H_2O 30°C	
	0.2%	Acetic Acid (1:5)	rotate – 15’
			Drain
	150%	H_2O 40°C	
	1%	Direct black dye	rotate – 15’
	4%	Protein-polymide polymer	rotate – 1 h
	1.5%	Sodium formiate	rotate – 10’
	1%	Soya lecithin	rotate – 10’
	1.5%	Sodium bicarbonate (1:5)	slowly
			rotate – 2 h (≠)
			pH = 5.2 – 5.4
			Drain
Dyeing	**50%**	H_2O 25°C	
	4%	Protein-polyamide polymer	
	2%	Prentration black dye	
	3%	Auxiliar synthetic	rotate – 2 h (≠)
			pH = 4.8 – 5.0
			Drain/Wash
Fatliquoring	**150%**	H_2O 60°C	
	3%	Soya lecithin	
	2%	Sulphonated beef tallow	
	4%	Oxi-sulphited marine oil	rotate – 1h
	0.7%	HCOOH (1:5)	rotate – 15’
			pH = 3.8 – 4.0

FINISHING FORMULATION

Coat	**75**	Pigment
	75	Wax
	75	Proteinic binder
	475	Water
	100	Acrylic resin
	100	Poliurethane 1
	100	Poliurethane 2
	4 x spraying machine (total dry 4 g/ft$^{2)}$ Press 80°C / 80 bar / 1"	
Top Coat	**200**	Top Poliurethane 1
	250	Top Poliurethane 2
	40	Silicone
	450	Water
	6	Cross-linker
	2 x spraying machine (total dry 0.5 g/ft$^{2)}$ Press 80°C / 80 bar / 1" Milling and toggling	