Study of the Effect of Temperature, Relative Humidity and UV Radiation on Wet-White Leather Ageing*

by

Anna Bacardit**, Mireia Cobos, Joaquim Font, Joan Jorge[1], Lluís Ollé
Igualada Engineering School (EEI). UPC.
Plaça del Rei, 15. 08700-Igualada (Spain)
[1]*Escola Politècnica Superior d'Enginyeria de Manresa (EPSEM). UPC.*
Av. Bases de Manresa, 61-73. 08240-Manresa (Spain)

Abstract

Since upholstery leather is considered a very high-tech product, a long service life is expected by the costumer. However, this type of leather can undergo extreme environmental conditions that may cause premature ageing. This work deals with the study of the effect of temperature, relative humidity, and UV radiation on leather ageing. Leathers with wet-white tannage were exposed to weathering effects using a climatic chamber in order to identify the most important variables affecting this weathering process and to check for interactions. Both a multilevel centralized factorial experimental design and an analysis of variance (ANOVA) have been employed as statistical tools for estimating the effects of the parameters.

Resumen

Ya que el cuero de tapicería es considerado como un producto de avanzada tecnología, una prolongada vida útil es esperada por el cliente usuario. Sin embargo, este tipo de cuero puede experimentar condiciones ambientales extremas que podrían causar envejecimiento prematuro. Esta obra se concierne con el estudio de los efectos de temperatura, humedad relativa, y radiación UV sobre el envejecimiento del cuero. Cueros con un curtido exento de cromo [wet-white] fueron expuestos a efectos del clima utilizando una recámara climática para así poder identificar las variables más importantes que afectan a este proceso de desgaste y para revisar las interacciones. Tanto un análisis centralizado factorial diseñado a multinivel y un análisis de la varianza (ANOVA) han sido utilizados como herramientas estadísticas para estimar los efectos de los parámetros.

*A **Technical Note** based on an oral presentation at the ALCA 106th Annual Meeting, Geneva, WI, June 10-13, 2010
**Corresponding author e-mail: annab@euetii.upc.edu
Manuscript received May 17, 2010, accepted for publication May 24, 2010

INTRODUCTION

Since upholstery leather is considered a very high-tech product, a service life of several years is expected by the costumer. However, this type of leather can undergo extreme environmental conditions that may cause premature ageing.[1-13]

The major 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 weathering test methods development.[14-18]

According to different studies carried out on historical/ancient leathers by leather conservation centers and museums, leather also is strongly affected by these three main environmental parameters: temperature, relative humidity, and UV radiation.[19-30]

Owing to the fact that the most part of these studies were centered on vegetable leather and semi-alum leather, in the present work we focus on the effect of these parameters on wet-white leather ageing. This type of tannage is increasingly used in the automotive sector following the European Union's Legislation on End of Life Vehicles and the market trends for chrome-free tanned leather.[31-32]

EXPERIMENTAL

Material

The tests were carried out on Spanish pickled cattle hides at pH = 3.2-3.5. The hides were tanned using tetrakishydroxymethylphosphonium sulphate (THPS) and silicate-phenolic synthetic. Next, the hides were neutralized at pH = 5.5 and retanned using 18% of protein-polyamide polymer. 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 of applying a base coat using pigment, oil, wax, acrylic resin, and two types of polyurethane (in total 3–4 dry grams of base coat per square foot of leather) by means of air spraying and pressing at 80˚C / 80 bar / 1". After that, the leathers were top coated using two types of polyurethane and crosslinker (in total 0.5 dry grams of top coat per square foot of leather) by means of air spraying and pressing at 80ºC / 80 bar / 1". Finally, the leathers were milled and toggled.

Methodology

The leathers were exposed during 7 days 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 interactions. A multilevel centralized factorial experimental design and an analysis of variance (ANOVA) have been 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 experimentation. 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	X_1	X_2	X_3	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 (in total 220 MJ/m^2) and for 2 days (in total 110 MJ/m^2) 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 in each of the properties analyzed.

By means of the Statgraphics Plus Program, the statistical analysis of the results obtained was carried out. The results of the main effects for the properties studied are graphed in Figure 1, showing the effect of relative humidity, temperature, and UV radiation factors analyzed in this experiment. The main effects' coefficients describe the individual influence of 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 = 79.4 + 0.0*T + 1.2*Hr - 0.1*UV + 0.6*T*Hr + 0.2*T*UV - 0.2*Hr*UV

b) Any factor was found significant in tear load.

c) Grain Distension = 15.20 - 0.59*T - 0.66*Hr - 0.35*UV - 0.26*T*Hr - 0.05*T*UV - 0.28*Hr*UV

d) Dry rubbing = 3.58 - 0.5*T - 1.12*Hr + 0.5*UV - 0.75*T*Hr - 0.37*T*UV + 0.25*Hr*UV

e) Wet rubbing = 3.16 - 0.62*T - 1.125*Hr + 0.375*UV - 0.5*T*Hr - 0.25*T*UV + 0.25*Hr*UV

f) Any factor was found significant in color loss.

g) Any factor was found significant in softness loss.

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	79.5	83.81	15.7	4	4-5	97.95	3.0
2	77.5	75.60	15.9	4-5	4	96.48	3.0
3	76.0	71.87	16.2	2	2	97.27	3.0
4	77.0	25.42	13.8	1	1	117.68	3.4
5	79.0	71.47	16.4	4-5	4-5	98.41	3.4
6	78.5	84.12	14.9	5	4-5	92.41	3.2
7	75.0	121.92	14.3	5	4-5	91.85	3.1
8	76.5	24.63	13.2	1	1	116.02	3.5
9	78.5	131.69	15.2	4	3	91.49	2.9
10	78.5	130.43	15.8	4	3	91.28	2.6
11	78.5	161.97	15.1	4	3	93.75	3.2
12	78.5	149.80	15.9	4	3	92.85	2.6

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

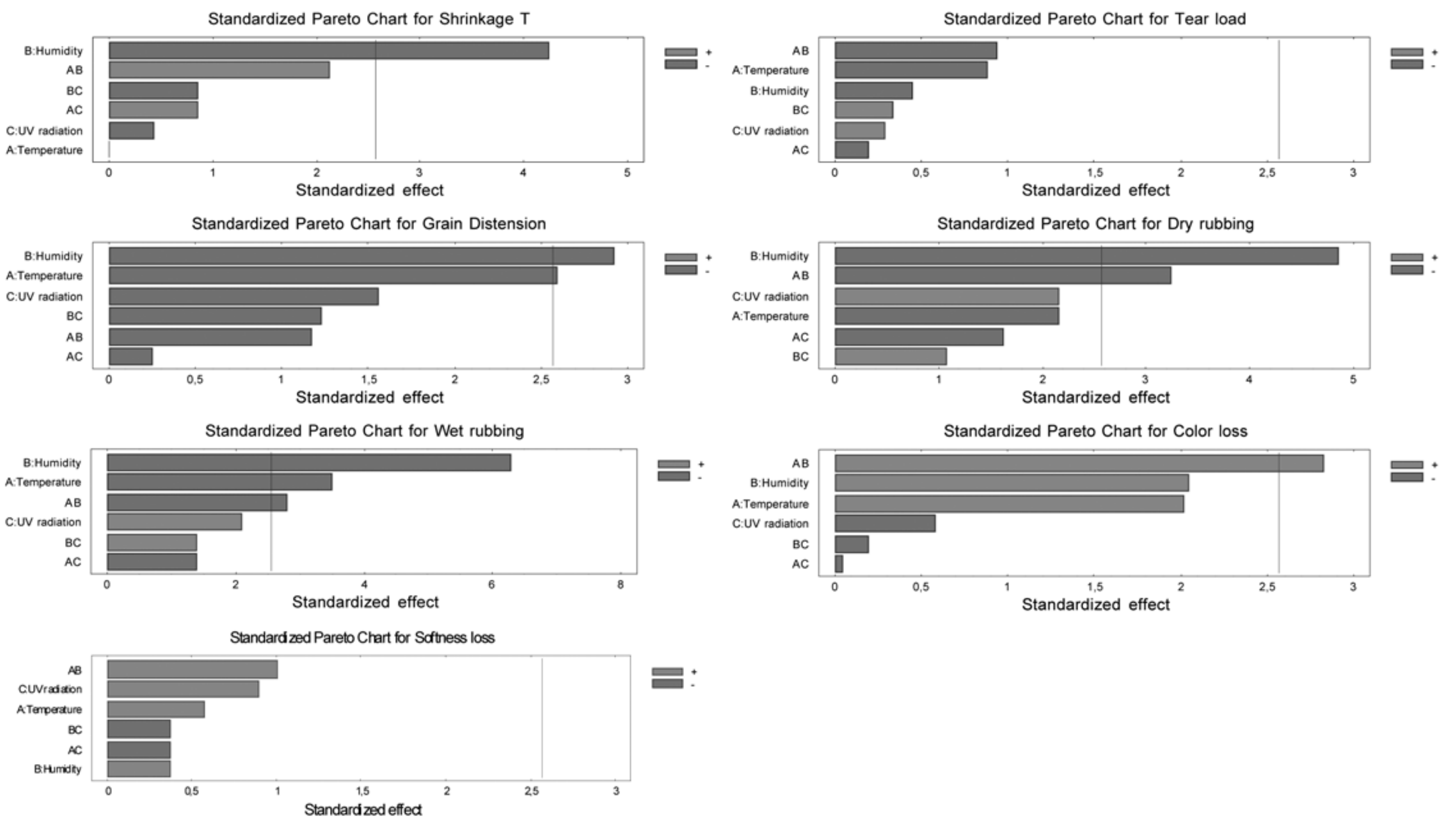

Figure 1. Statistical analysis of the effect of the weathering variables on physical and fastness properties.

The analysis reveals several critical observations: relative humidity has, by far, the largest effect on all properties studied except for the tear load, color loss, and softness loss, in which any factor was found significant. Temperature also shows a significant effect on grain distension and wet rubbing. The analysis also indicates the possibility of a two-way interaction between relative humidity and temperature. However, this effect appears only in dry rubbing, wet rubbing, and color loss.

As investigated in previous studies,[31-35] the resistance and dimensional stability of WW leathers is higher than that of chrome-tanned leathers. Wet-white leather and chrome-tanned leather show a different behavior to leather ageing. As reported in previous studies of natural weathering,[32,33] loss in properties in chrome-tanned leather increases steadily until 40 days exposure, and after this point the leather stabilizes and no longer degrades. In wet-white leather, however, there is a progressive loss in properties but stabilization does not occur until a period of exposure of 80–120 days.

This said, wet-white leathers have a disadvantage: they are not resistant to simultaneous exposure to high temperatures and high relative humidity.[31,35] The comparative study of the properties of the samples exposed to natural weathering conditions and those exposed to tropical environmental conditions shows that after 7 days exposure the latter conditions resulted in greater ageing than those of the former after an exposure of 80 days but lower than an exposure of 120 days. However, a further extension of 14 days caused a very acute loss of leather properties, setting off the carbonization process that lasted until a total exposure of 21 days.

Another interesting point is that contrary to what occurred in the natural weathering study, the analysis of variance did not reveal any significant factors in softness loss. This is so because during the exposure in an enclosed chamber, the fat released through ageing does not volatilize and is deposited on the leather surface instead. For this reason, also the tests with high humidity (tests 4 and 8) do not result in color loss; the samples turn darker instead (see Table II).

In addition, neither of the properties are affected by UV radiation. This may be due to the fact that the substances that act as tans and retans are not much rich in chromophore groups likely to absorb energy in the form of light. This is contrary to what occurs with vegetable tannins, since these substances are highly absorbing due to their conjugated phenyl rings. To this regard, it is likely that a wet-white formulation with a vegetable retanning would have produced very different results. It is well-know how, in the context of the leather cultural heritage, exposure to light of mostly vegetably tanned historical leathers causes an acute decrease of shrinkage temperature and a worsening of sensory properties.[36] On the other hand, chrome complexes, like those of other transition metals, demonstrate high absorbance capacity in the UV-VIS spectra. Therefore, it makes sense that the chrome-collagen complex absorbs energy when chrome-tanned leathers are exposed to UV light, which affects their own stability over time.

3.2. 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) $IR = 0.29 - 0.03*T - 0.05*Hr + 0.01*UV - 0.06*T*Hr - 0.01*T*UV + 0.002*Hr*UV$

i) $\text{Water soluble inorganics} = 0.52 + 0.07*T + 0.07*Hr + 0.03*UV + 0.03*T*Hr - 0.05*T*UV + 0.006*Hr*UV$

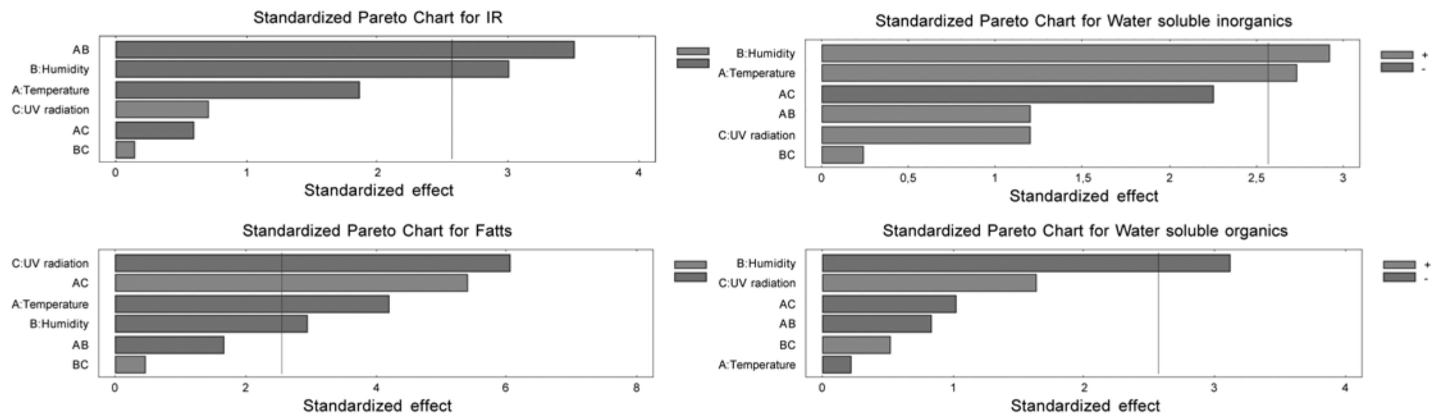

Figure 2. Statistical analysis of the effect of the weathering variables on modification of the leather composition.

TABLE III

Effect of the weathering variables on modification of the leather composition

TEST	IR*	Water soluble organics %	Water soluble inorganics %	Fats %
1	0.2948	1.22	0.35	16.74
2	0.3523	1.25	0.54	10.79
3	0.2802	0.89	0.42	15.20
4	0.1291	0.99	0.75	7.48
5	0.3107	1.29	0.51	7.95
6	0.3826	1.36	0.48	10.29
7	0.3676	1.25	0.62	7.65
8	0.1066	0.98	0.70	7.04
9	0.3343	1.12	0.44	9.96
10	0.3011	0.96	0.40	10.56
11	0.3617	1.03	0.51	11.39
12	0.3637	1.07	0.55	8.43

**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* = $Abs_{2923\ cm-1} + Abs_{1730\ cm-1} + Abs_{798\ cm-1}$)

j) Water soluble organics = 1.11 - 0.008*T - 0.12*Hr + 0.06*UV - 0.03*T*Hr - 0.04*T*UV + 0.02*Hr*UV

k) Fats = 10.29 - 1.49*T - 1.05*Hr - 2.16*UV - 0.59*T*Hr + 1.925*T*UV + 0.16*Hr*UV

[NOTE: Contact the editor or authors for reproduction of Figs. 1 and 2 in original color.]

The analysis confirms again that relative humidity was found significant on all of the properties analyzed. Temperature shows a significant effect on water soluble inorganics, IR, and fats.

Through the analysis of variance for matter soluble in dichloromethane, it was observed that it is the only property affected by UV radiation, and emerges as the most important one. It is known how insaturated oils form free radicals when exposed to light.[9,10,12-13] 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 of all the components in the WW leather.

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., 0°C, 0% Hr, and without UV radiation).

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

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

A 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.

CONCLUSIONS

The aim of this study was to examine the effect of the temperature, relative humidity, and UV radiation on wet-white leather ageing. Relative humidity 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. Temperature showed also a significant effect on most of the properties under study. The analysis indicated the possibility of a two-way interaction between relative humidity and temperature. In contrast, UV radiation showed only a marginal effect. Indeed, Determination of matter soluble in dichloromethane is the only property affected by UV radiation since the fattening agents are the components that are most sensitive to the effect of light of all the components in a wet-white leather.

Resistance and dimensional stability of WW leather both in accelerated ageing tests and natural weathering exposure is higher than that of chrome-tanned leather. For this reason, WW leathers are used a lot in automotive upholstery. However, these leathers have the disadvantage of not resisting simultaneous exposure to high temperatures and high relative humidity, that's to say, tropical environmental conditions. No correlation has been found between ageing caused by natural weathering and that caused under controlled conditions in the laboratory.

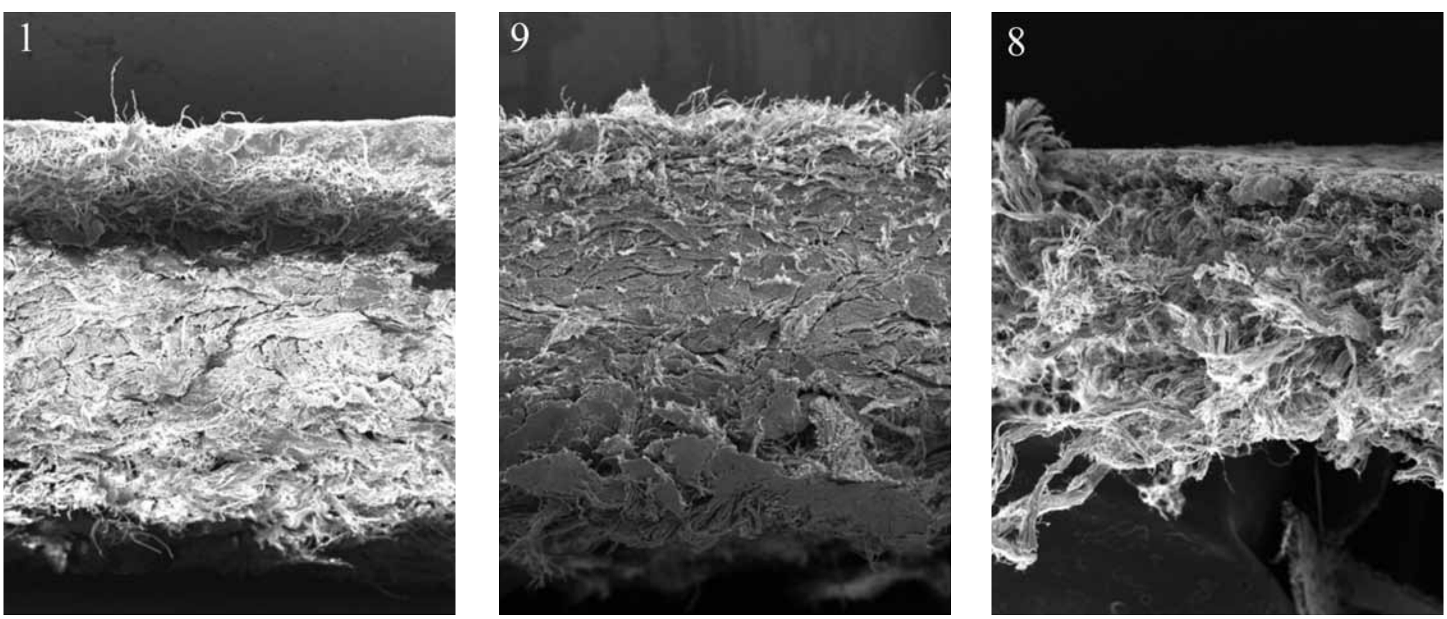

Figure 3. Micrograph (SEM) of cross-section of leather samples no. 1, 9, and 8.

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, J. Soc. Leath. Tech. Ch., **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, *J. Soc. Leath. Tech. Ch.* **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, Spain, 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, Spain, 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, Spain, 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 behaviour 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 Centre. 1991
21. Bowes, J.H.; Raistrick, A.S.; The action of heat and moisture on leather. V. Chemical changes in collagen and tanned collagen, *J. Soc. Leath. Tech. Ch.* **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 Center, 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 Center, 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 Center. 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, *J. Soc. Leath. Tech. Ch.* **77**, 151, 1993
30. Thomson, R.; Conserving historical leathers: Saving our past for the future, *JALCA* **97**, 307, 2002
31. Wolf, G.; Breth, M.; Carle, J.; Igl, G.; New developments in wet white tanning technology, *JALCA* **96**, 111, 2001.
32. Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of life vehicles.
33. Bacardit, A.; Ollé, L.; Font, J.; Cobos, M.; Morera, J.M.; Bartolí, E.; Natural weathering study of a coating for upholstery leather, 105th. Annual Meeting of ALCA, Wheeling, WV, 2009.
34. Bacardit, A.; Cobos, M.; Font, J.; Ollé, L.; Study of the leather aging due to natural weathering, in Proceedings of the 59º congreso AQEIC, Arnedo—La Rioja, Spain, 2010.

35. Ollé, L.; Cobos, M.; Font, J.; Bacardit, A.; Comparison of leather aging due to tropical environment exposure and natural weathering, in Proceedings of the 59º congreso AQEIC, Arnedo—La Rioja, Spain, 2010.

36. 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, *J. Soc. Leath. Tech. Ch.***94**, 59, 2010.