Paper B21

Comparison of the weathering variables on both chrome-tanned and wet-white leather ageing

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Abstract
Leather is a natural material that can be used in different environments and often under aggressive environmental conditions that may cause premature ageing. The most important factors influencing the degradation of leather are temperature, relative humidity and UV radiation. Leathers with chrome tannage and wet-white leathers 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.

1. Introduction
As reported in previous studies, leather is strongly affected by three main environmental parameters: temperature, relative humidity and UV radiation [1-12].
When leather is exposed to sunlight or high temperatures, it absorbs energy which induces photochemical reactions by radical mechanisms. Firstly, chemical compounds split off and free radicals are formed. Secondly, these radicals react immediately with oxygen to form peroxide radicals. Peroxide radicals further react with the organic constituents of leather, and dyes, tanning agents and fatliquors, breaking some of the bonds between the said products and collagen[13-15]. It is known how insaturated oils form free radicals when exposed to light[16-19].
Results obtained in previous studies showed a different behaviour of both types of leather (i.e. chrome-tanned and wet-white) to leather ageing. As reported by G. Wolf et al., the resistance and dimensional stability of wet-white leathers is higher than that of chrome-tanned leathers. Therefore, wet-white 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 [20,21]. However, wet-white leather cannot withstand the simultaneous exposure to high temperatures and high relative humidity[22-25].

2. Experimental
2.1. Material
The tests were carried out on Spanish pickled cattle hides at pH = 3.2 – 3.5. Two types of tanned leather were tested: on the one hand, chrome tanned leather and on the other hand, wet-white tanned leather. In the latter case, the hides were tanned using tetrakishydroxymethylphosphonium sulphate (THPS) and silicate-phenolic synthetic. In both types of tanned leather, the hides were neutralized at pH = 5.3 and retanned using synthetic agents and resins; in wet-white hides, a total amount of 18% of protein-polyamide polymer was added as a retan agent. Then, the hides were 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 ºC / 80 bar / 1". Afterwards, 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 80 ºC / 80 bar / 1”. Finally, the leathers were milled and toggled.

2.2. 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	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 (220 MJ/m2 in total) and for 2 days (110 MJ/m2 in total) using a Suntest XLS+ Atlas equipped with a xenon lamp and window glass filter.

2.3. 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.

3. Results and discussion

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

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 on chrome tanned leather 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.

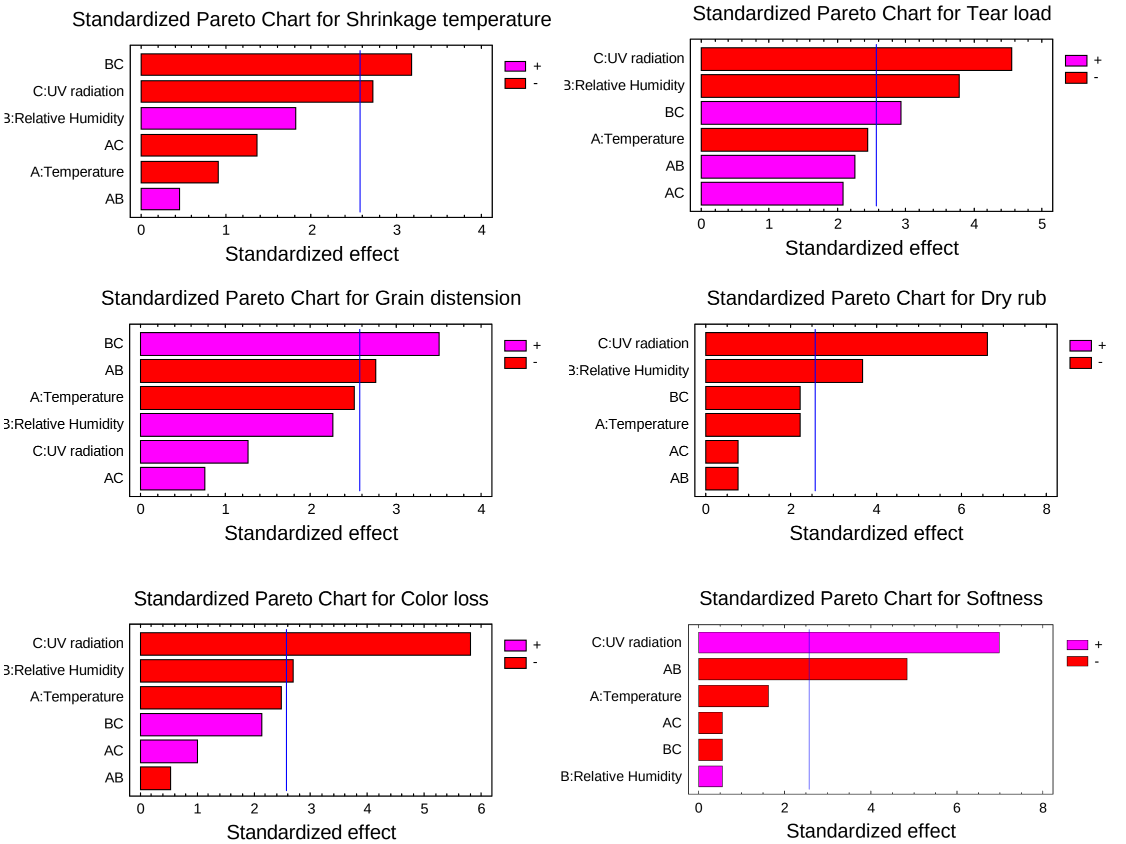

Figure 1. - Statistical analysis of the effect of the weathering variables on physical and fastness properties of chrome tanned leather

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 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.

The results of the main effects for each of the properties studied on wet-white leather are graphed in Figure 2.

These results reveal 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.

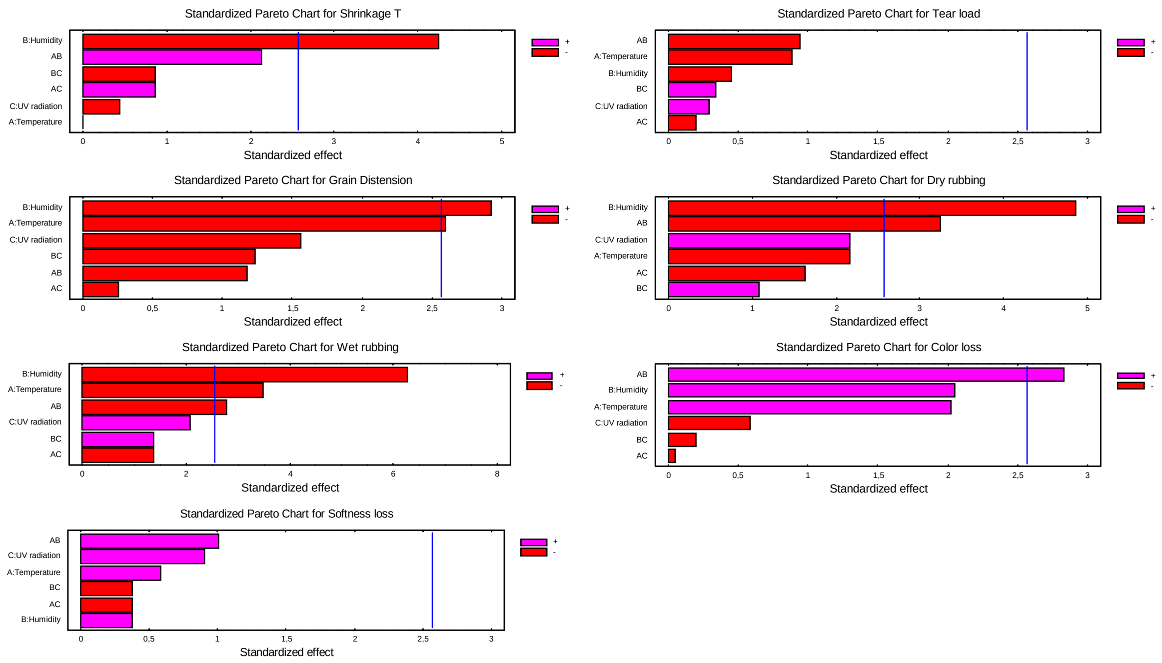

Figure 2. - Statistical analysis of the effect of the weathering variables on physical and fastness properties of wet-white leather

As reported in previous studies[22-24], 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.

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

In order to compare the chemical degradation of leather due to temperature, relative humidity and UV radiation, the following was determined: matter soluble in dichloromethane, water soluble inorganic matter, water soluble organic matter and IR spectra.

For each of the studied properties, the standardized Pareto chart for chrome tanned leather is shown in Figure 3. Figure 4 shows the Pareto chart for wet-white leather.

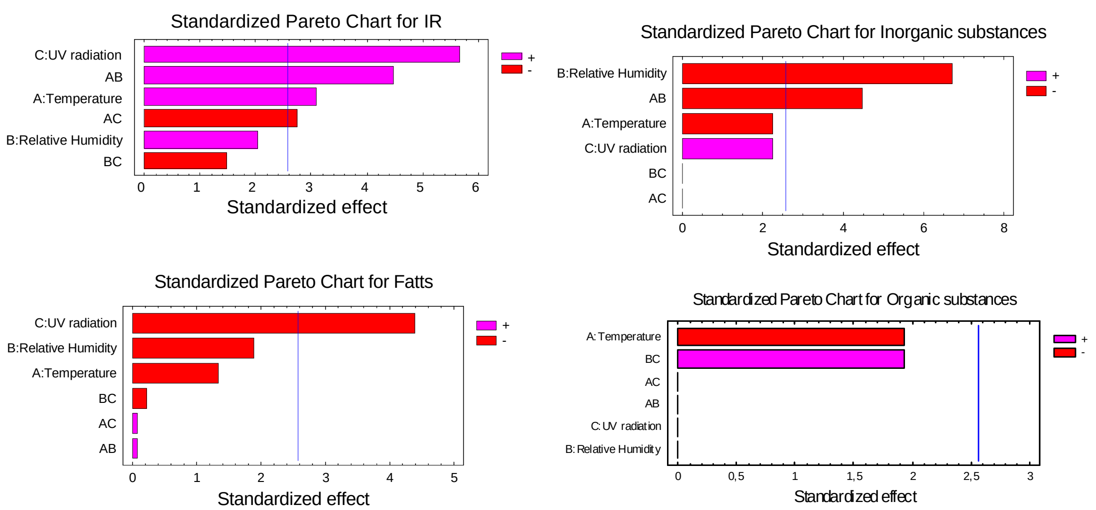

Figure 3. - Statistical analysis of the effect of the weathering variables on modification of the leather composition for chrome tanned leather

As can be seen in the Pareto charts shown in Figure 3, 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.

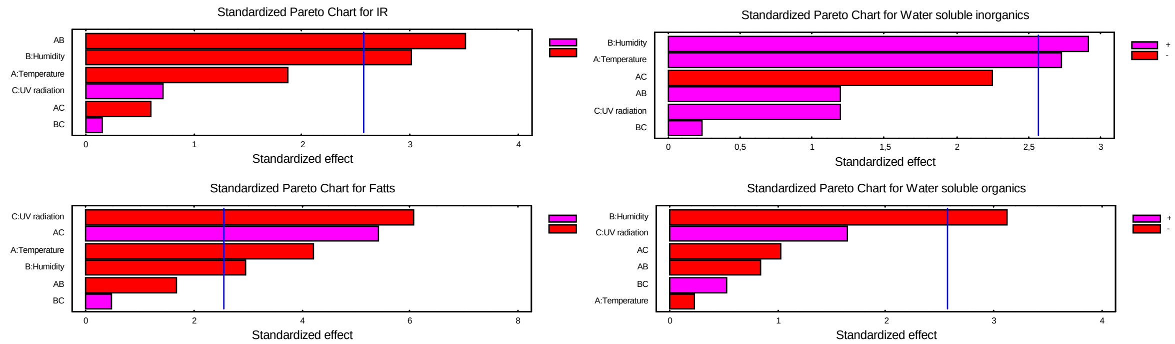

Figure 4. - Statistical analysis of the effect of the weathering variables on modification of the leather composition for wet-white leathers

The results show a different behaviour of both types of tanned leather under the studied weathering variables. The analysis confirms again that relative humidity was found significant on all of the properties analyzed in wet-white leathers. 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[13-19]. 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.

3.3. Changes in fibrous structure

Figure 5 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/m2).
Sample no.8 was exposed to high settings for each factor (i.e., 70ºC, 95% Hr, and 220 MJ/m2).

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.

4. Conclusions

The aim of this study was to compare the effect of the temperature, relative humidity, and UV radiation on chrome-tanned leather and wet-white leather ageing. UV radiation was the factor with the highest impact on most of the properties analyzed on chrome-tanned leather. Therefore, it plays a key role in weathering and consequently in chrome-tanned 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.

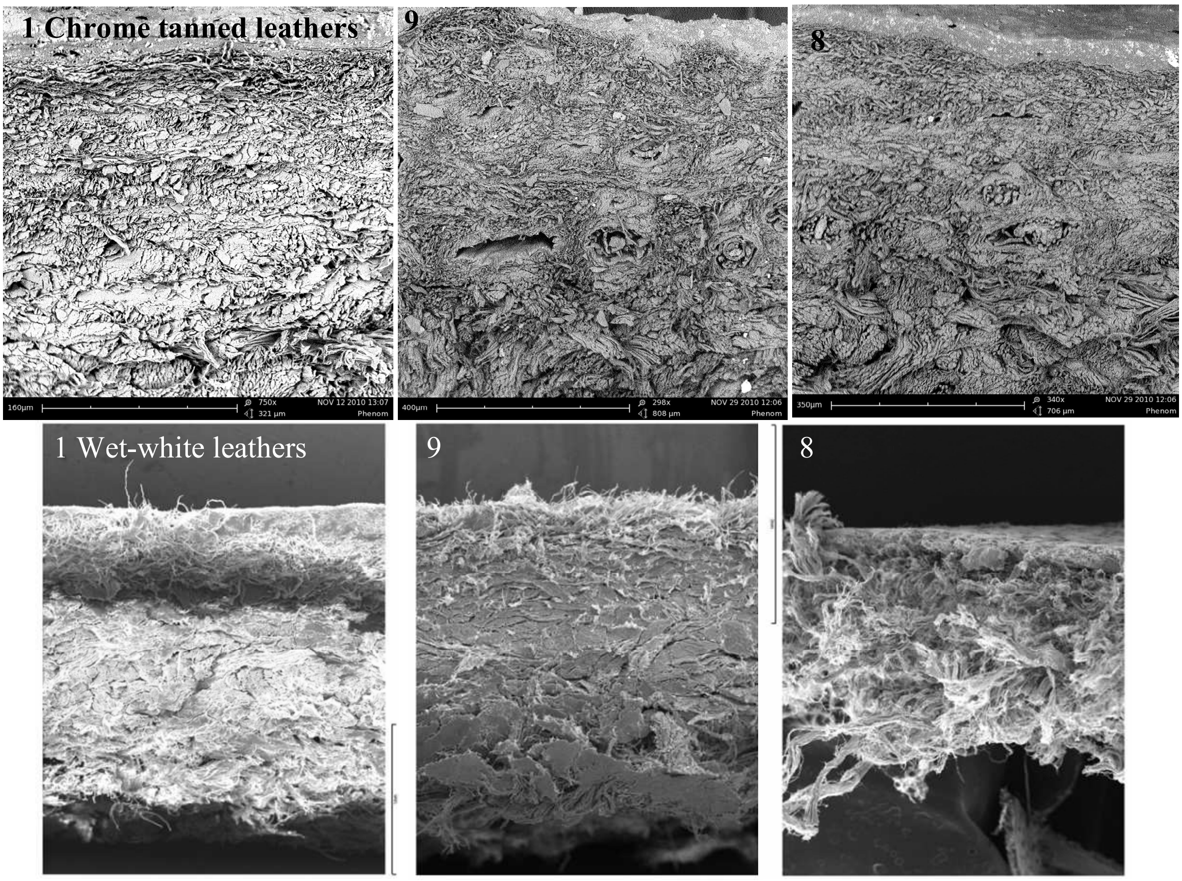

Figure 5. – Micrograph (SEM) of cross-section of leather samples no.1, 9, and 8

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