EFFECT OF FATLIQUORING AND FINISHING ON MOISTURE ABSORPTION-DESORPTION OF LEATHER

A. M. Manich¹, J. Barenys², L. Martínez², M. Martí³, J. Carilla¹, A. Marsal¹

¹IQAC-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain
²TRUMPLER Española S. A., carrer Llobateres 15, Barberà del Vallès
Corresponding author: A. M. Manich; albert.manich@iqac.csic.es

Abstract

The comfort of leather is a relevant aspect that makes the end user select this material instead of other alternative materials. This comfort depends largely on the physical, mechanical and organoleptic characteristics of the finished leather including its moisture absorption/desorption behaviour. Among the post-tanning operations, fatliquoring and retanning plays a great influence on the properties of leather, especially those related to handle. In this work, the influence of fatliquoring and finishing on the leather moisture absorption-desorption is studied.

The experimental work was performed at the pilot plant of Trumpler Española S.A., using wet-blue leathers from Ireland as starting material, which were shaved to a thickness of 1.2-1.4 mm. After washing, rechroming and neutralization, leathers were retanned and dyed following a conventional process and then, they were fatliquored with five different fatliquors provided by the company (a combination of sulphited triglycerides of colza oil and fatty polymer TCSi/PGR used as reference treatment, their components TCSi and PGR, phosphoric ester ESF and sulphited fish oil PSi). A 7% of active matter (on shaved weight) was applied. After a final washing, a sample of the treated leathers was kept in “crust” state (without finishing), and the rest received a light finishing process following a conventional recipe.

The absorption/desorption of moisture in a substrate is a dynamic process that involves long periods of time to reach equilibrium when water molecules are linked to all sorption sites. The monolayer consists of the moisture directly linked to the sorption sites of the substrate (primary water strongly bonded), while moisture linked through the monolayer forms the multilayer weakly linked to the substrate (secondary water). It is expected that fatliquoring and finishing modify the accessibility of moisture into leather. Experiments of moisture absorption/desorption are made according to the following steps:

Criteria of equilibrium: To shorten the absorption and desorption processes, we consider that the sample reaches the equilibrium with the environment when its variation in mass is lower than 0.02% for 10 min.

Dry weight of the sample: The dry weight of the sample to which moisture gains and losses will be referred, is obtained after an initial drying step at 60°C and 0% RH.
(relative humidity). The step is applied for 60 min unless the sample attains the equilibrium criteria before.

Initial step of absorption: Dried sample is subjected to an atmosphere of 25ºC and 5% RH for a maximum period of 500 min unless the sample attains the equilibrium criteria before.

Absorption steps: After the initial step of absorption the sample is subjected to growing relative humidity environments from 5% to 95% of RH. The variation in mass is recorded along the steps of 5, 15, 25, 35, 55, 75 and 95% RH for a maximum period of 500 min unless the sample attains the equilibrium criteria before.

Desorption steps: Sample equilibrated in the environment of 25ºC and 95% RH is subjected to a decreasing relative humidity environments from 95% to 5% along the steps of 75, 55, 35, 25, 15 and 5% RH for a maximum period of 500 min unless the sample attains the equilibrium criteria before.

Sample water content: the amount of water absorbed/desorbed in each step is expressed as percentage of the sample dry weight (regain) X.

Environment water vapour content: The ratio of the actual pressure of the water vapour in the atmosphere to the saturation pressure of water vapour at the same temperature is known as activity of water aw, that when expressed as a percentage is known as Relative Humidity RH, (aw = RH/100).

Modelling the Absorption/Desorption Isotherm

Using the final water content of the sample at each step when the equilibrium is reached, the Guggenheim, Anderson and de Boer (GAB) model has been fitted to derive the characteristic parameters of each sample.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>aw</td>
<td>Water activity of the environment to which the sample is subjected</td>
</tr>
<tr>
<td>X</td>
<td>Sample water content (regain % odb) when the equilibrium is reached.</td>
</tr>
<tr>
<td>Xm</td>
<td>Monolayer moisture content. This is the primary water directly linked to the sample forming the monolayer (regain % odb).</td>
</tr>
<tr>
<td>C</td>
<td>Energy constant of the monolayer. This is proportional to the rate between both the attachment and the escape rate constants for the primary sites.</td>
</tr>
<tr>
<td>K</td>
<td>Energy constant of the secondary layers. Proportional to the rate between the attachment rate constant and the escape rate for all higher layers.</td>
</tr>
</tbody>
</table>
Moisture Diffusion kinetics

The Vickerstaff method used to determine the diffusion coefficient of dyes in fibres has been applied to study the diffusion coefficient of moisture in absorption and desorption along the different steps. At each step of sorption and desorption the half sorption/desorption regain \( X_{1/2} \) and the corresponding half sorption/desorption time \( t_{1/2} \) have been determined and the rate \( X_{1/2}/t_{1/2} \) yields the half sorption/desorption rate at each step. At each step the evolution of the relationship \( X(t)/X \) in function of the \( \sqrt{t} \) enabled us to derive an apparent coefficient of diffusion \( D_A \) following the Fick’s model that can be obtained when the geometrical form of the sample is not considered. In this work the coefficient of diffusion is based on the % of moisture sorbed/desorbed by the sample per unit of time.

\[
X(t)/X = \sqrt{D_A \cdot \sqrt{t}}
\]

Hysteresis

The representation of the hysteresis in function of the water activity points out the energy at which water adsorbed at this humidity level is linked on the substrate. As is expected, the higher the moisture relative humidity, the lower the bonding energy of moisture with fibre because the probability to be secondary water increases with relative humidity. At lower water activity the probability to be primary linked water ascends. The comparison of the regain in desorption \( X_d \) with the regain in adsorption \( X_a \) at different humidity levels yields the hysteresis at this humidity level:

\[
\text{Hyst} \ (\%) = 100 \times \frac{(X_d - X_a)}{X_a}
\]

Conclusions

Fatliquoring mainly affects the maximum sorption capacity of the leather although the size of the monolayer capacity is slightly affected by this process. Fatliquoring also decreases the monolayer capacity while makes the energy constant of the monolayer increase.

There are significant differences between fatliquors as regards the apparent coefficient of diffusion. The highest coefficients were those attained by of sulphited triglycerides of colza oil and sulphited fish oil while the lowest were those given by the non fatliquored leather and that fatliquored by the combination of sulphited triglycerides of colza oil and fatty polymer.

As regards the effect of finishing according to the relative humidity, finishing enhances the diffusion coefficient in the intermediate range of humidity 30 to 65% while differences are decreased at the extreme values.

Up to 25% of relative humidity that concerns with primary water the diffusion coefficient in absorption is greater than that of desorption while at higher humidity
levels which are related with secondary water the coefficients in desorption are being greater than those in absorption as humidity increases.

Acknowledgement

The authors wish to thank the CTQ2013-43029 Project for the financial support.