

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

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Abstract

The purpose of the paper is to investigate the moisture absorption-desorption kinetics of leather, a natural collagen fibrous structure, by the application of Vickerstaff's method that enables to determine the diffusion coefficient of dyes in fibres, to the diffusion coefficient of moisture in leather. Leather has been fatliquored and finished in order to evaluate the effect of these treatments on moisture diffusion. Samples were subjected to ascending and descending steps of relative humidity, to cause absorption/desorption of moisture in leather. The amount of moisture absorbed/desorbed is measured as regain (% odw). At each step the final regain (at equilibrium) X , the half absorption/desorption time $t_{1/2}$, the ratio $X^{1/2}/t_{1/2}$ being $X^{1/2}=X/2$ that corresponds to the diffusion rate were calculated. Following Vickerstaff's method the maximum slope of the normalized absorption plot $X(t)/X$ vs. \sqrt{t} enabled us to derive the square root of the apparent coefficient of diffusion DA which is based on the % of moisture absorbed/desorbed by a unit of sample mass per unit of time.

Hysteresis depends on the water activity (RH%/100) of the environment and points out the energy at which the moisture absorbed at this humidity level is linked to the substrate. The higher the relative humidity, the lower the bonding energy of moisture. At lower water activities the absorbed moisture is linked to collagen as primary water. The comparison of the regain in desorption X_d vs. regain in sorption X_a at different humidity levels yields the hysteresis at each humidity level: $Hyst (\%) = 100 * (X_d - X_a) / X_a$.

Fatliquors mainly affect the maximum sorption capacity of leather, decrease the size

of the monolayer although makes to ascend the bonding energy. Significant differences in the apparent diffusion coefficients between fatliquors have been observed. The highest coefficients were those 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 humidities between 30 and 65% while differences decrease at the extreme values.

Keywords: leather, collagen, fatliquoring, finishing, moisture, absorption, desorption, diffusion coefficient, hysteresis, sulphited triglycerides of colza oil, sulphited fish oil, fatty polymer.

1 Introduction

When collagen is placed in a given atmosphere, it acts as a moisture buffering body that gradually takes up or loses water until reaching equilibrium. This is a dynamic equilibrium that occurs when the number of water molecules evaporating from the specimen in a given time equals the number of water molecules absorbed. The moisture content of collagen/leather influences its properties [1, 2, 3], can develop driving forces causing spatial displacement of the substrate [4] and, by over drying, leather properties are modified in an irreversible way [5, 6]. The property of absorbing moisture is a valuable characteristic of articles in contact with the human body. This avoids problems caused by accumulation of sweat on the skin and in shoes [7]. The sorption of water causes the leather to act as a heat reservoir, protecting

the body from sudden changes in external conditions. The moisture buffering ability of leather is determinant in comfort feeling and, when used in upholstery, enhances the indoor air quality of a room [8]. Moisture content affects its microbial resistance, aspect and durability [9].

The fibrous structure and the large concentrations of hydrophilic groups of collagen account for its high water sorption capacity. In a study on water-collagen interactions using rat-tail tendons, Pineri et al. [10] described different mechanisms of water fixation. Grigera et al. [11] reported two types of water. One type of water is hydrogen-bonded to the macromolecular backbone at well-defined positions and the other type interacts weakly with a number of different sites, forming a multilayer with more liquid-like properties. This is consistent with the view of Caurie [12], who described three types of water: a) water adsorbed onto the most energetic sites known as strongly bonded primary sites, b) water consisting of weakly bonded secondary molecules, and c) unbounded free liquid water that condenses at saturation pressure.

Sorption isotherms

It is common knowledge that there is a good correlation between the number of water molecules in a monolayer and the number of polar side chains using the classic Brunauer, Emmett and Teller (BET) multilayer sorption equation. This suggests that each polar group initially sorbs one molecule of water followed by multimolecular sorption at a higher humidity. Despite its limitations, BET equation is still used to calculate monolayer values in very different physicochemical fields, yielding data sorption specific area values. The BET equation is used because of its simplicity and because it has been approved by the International Union of Pure and Applied Chemistry (IUPAC). In 1985, the Commission on Colloid and Surface Chemistry recommended the so-called BET plot for a standard evaluation of monolayer values in the relative vapour pressure (water activity) interval between 0.05 and 0.30.

The Guggenheim, Andersen and de Boer (GAB) sorption equation also provides monolayer sorption values. It has become more popular because the range of the

relative vapour pressure interval is much wider than that of the BET equation (from 0.05 to 0.8-0.9) [13]. The BET and the GAB isotherms are closely related since they are based on the same statistical model. The GAB, which is an improvement on the BET model, shares with it the two original BET constants: a) the monolayer capacity X_m , and b) the energy constant C . The GAB model owes its greater versatility to the introduction of a third constant K .

The energy constants determine the sigmoid shape of the isotherms. Constant C determines the shape of the "knee" at the lower activity range and is proportional to the ratio between the attachment rate constant and the escape rate constant per unit pressure for the primary sites [13]. Constant K determines the profile at the higher water activity range, regulating the upswing after the plateau following the "knee" at the medium water activity range, and is related to the attachment rate constant and the escape rate for all higher layers in the system [14]. The lower the value of K , the less structured the state of the sorbate in the multilayers above the monolayer, which is less structured than in the pure liquid state. K increases with stronger interactions between sorbate and sorbent [13].

Hysteresis gives rise to two different paths between sorption and desorption. The extent of it is related to the nature and state of the components of the sample, reflecting their potential for structural and conformational rearrangements, which alter the accessibility of the water to the energetically favourable polar sites [15]. The general shape of the equilibrium water sorption isotherm for collagen can be described by a Type II or Type III isotherm with a small amount of water that persists at a very low relative humidity and a large amount of water at a high relative humidity [16]. Table 1 shows the sorption isotherms and the parameters used to fit the experimental sorption/desorption data.

The basic mechanism of equilibrium depends on the balance between the rate of attachment and detachment of water molecules in the sorbed material. The monolayer moisture content calculated from the equilibrium sorption isotherms is essential for the physical and chemical stability of dehydrated materials. At lower water activities water is held by strong hydrophilic sites. When sorbed, water

molecules can become attached to additional water molecules that are transformed into less firm sorption sites. When the water activity is increased, sorption enters a second region, where sorbed water is more loosely held by hydrogen bonds. This “multilayer region” can be considered a transition phase between the initial and final regions of the isotherm. The least firmly bonded water is produced when the water activity attains the highest levels. In this region, “condensed water” is mechanically entrapped within the voids of the fibre, and has many of the characteristics of liquid water. According to Dent [14] it is possible to calculate the fractions of the total sorption as a function of water activity a_w : variation of empty sites, monolayer moisture content, “primary” and “secondary” water bonded molecules, and the ratio between them.

Table 1: BET and GAB models. Parameters used to fit the experimental sorption data

Model	Mathematical equation
BET [21]	$X = X_m C a_w / [(1-a_w)(1-a_w+C a_w)]$
GAB [22]	$X = X_m C K a_w / [(1- K a_w)(1- K a_w+C K a_w)]$
Parameter	Definition
a_w	Water activity expressed as vapour relative pressure p/p_0 , where p_0 is the saturated vapour pressure.
X	Equilibrium moisture content at a_w in g sorbed/100 g of sorbent on dry basis.
X_m	Monolayer moisture content in g sorbed/100 g of sorbent on dry basis d.b.
C	Energy constant related to the difference between the free enthalpy of the water molecules in the pure liquid state and in the monolayer. This is proportional to the rate between both the attachment and the escape rate constants for the primary sites.

K	Ratio between the standard vapour pressure of the liquid and the vapour pressure of the sorbate in the secondary (upper) layers. Proportional to the rate between the attachment rate constant and the escape rate for all higher layers.
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Among the post-tanning operations, fatliquoring, together with retanning, is one of the most influencing treatments on leather characteristics, in particular those related to handle and comfort [17, 18]. Fatliquors are added to leather for similar reasons as plasticizers to polymers (the improvement of their flow properties) [19], enhances fiber mobility due to the reduction of the friction between microfibrils [20] and prevents fiber adhesion by filling the spaces between the network structure, resulting in a greater fiber mobility [20]. Fatliquors are placed between collagen fibrils and act as lubricant, improving handle and making easy the relative displacement of microfibrils when are subjected to mechanical stresses. Fatliquors modify the size of the leather internal sorbing surface of moisture, affecting their comfort feeling.

Objective

The main aim of this study is to evaluate the absorption/desorption behaviour of leather explained by the half adsorption/desorption rate, the apparent coefficient of diffusion and their relationships according to fatliquoring, finishing, test mode (adsorption/desorption) and relative humidity.

2 EXPERIMENTAL

MATERIALS

The experimental work was carried out at the pilot plant of Trumpler Española SA. Wet-blue sides from Ireland, shaved to a thickness of 1.2-1.4 mm, were used. After washing, rechroming and neutralization, leathers were retanned and dyed following a conventional process and, then, they were fatliquored with five fatliquoring agents of different chemical composition in order to compare their effect on moisture absorption/desorption. Fatliquoring was carried out by applying a 7 % of active matter on shaved weight. After a final

washing and drying, moisture absorption/desorption tests were carried out. To evaluate the effect of finishing, a light standard finishing was applied to each of the samples. Results before and after finishing were compared with those of the non fatliquored sample before and after finishing.

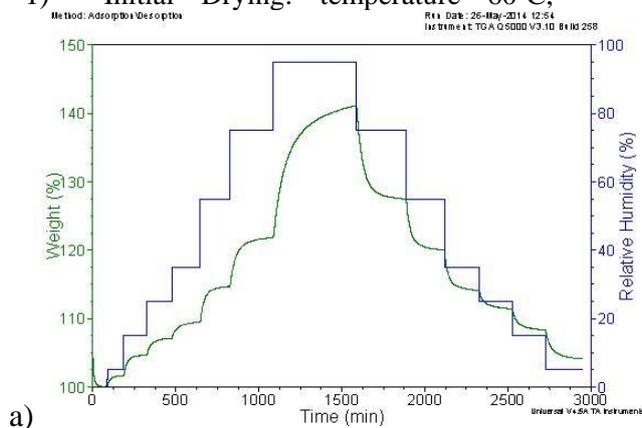
Fatliquors were identified by their main characteristic component:

- Sulphited triglycerides of rapeseed oil TCSi
- Fatty Polymers (non water repellent) PGR
- Phosphoric Ester ESF
- Sulphited fish oil PSi
- The standard fatliquoring agent used as reference is the combination (TCSi/PGR).

METHODS

Sorption and desorption plots of samples around 12 mg in mass were measured for moisture absorption/desorption by the Q5000SA Dynamic Vapour Sorption DVS Analyzer (TA Instruments), according to the following procedure:

- 1) Initial Drying: temperature 60°C,



relative humidity 0%, time 1 h.

- 2) Pre-stabilization: temperature 25°C, relative humidity RH 0% and then, initial adsorption at RH 5%.

- 3) Sorption steps: the sample previously stabilized at 5% RH is subjected to absorption tests that progressively increase from 15% to 25%, 35%, 55%, 75% and 95% of RH.

- 4) Desorption steps: the sample stabilized at 95% RH after the sorption kinetics is subjected to desorption tests that progressively decrease from 75% to 55%, 35%, 25%, 15% and 5%.

- 5) Final step conditions: each step lasts a maximum time of 500 min. If variation in weight is lower than 0.02% for 10 min, the step is considered that has reached a quasi-equilibrium condition.

Based on the moisture content at the end of each step, the software provided by TA Instruments fits the BET and GAB models to the experimental data. Figure 1 shows the results of the absorption/desorption test and the isothermal plot using final regains at each step.

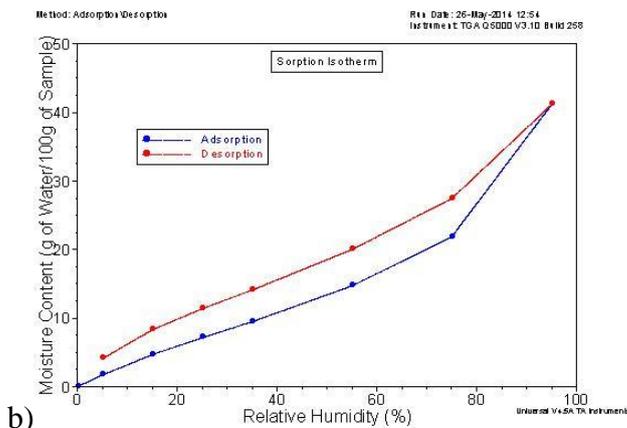


Figure 1 a) Sample mass variation in (% odw) at different relative humidity levels of absorption/desorption according to measuring procedure; b) Absorption/desorption isotherm using the final regain of each step.

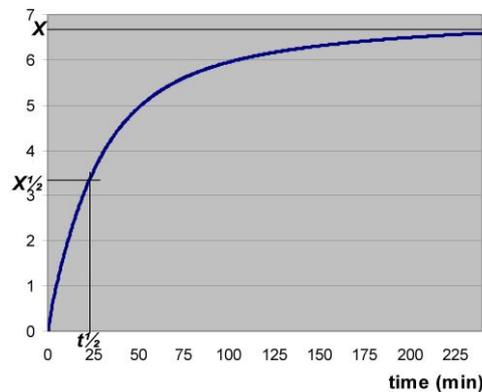
The complete description of the absorption phenomena under particular conditions of temperature and relative humidity under which the sample is placed, is completely described by the sorption isotherm vs. time plot. It normally shows an initially rapid absorption/desorption which tends asymptotically towards the equilibrium. The main feature of the plot describes the gain or loss of regain at quasi-equilibrium X and the rate at which this is achieved. The absorption/desorption rate can be numerically characterized by the time of half-sorption $t_{1/2}$ which is the time required for the substrate to absorb/desorb half as much regain $X_{1/2}$ that is interchanged with the environment when the quasi-equilibrium conditions are reached. The rate of half sorption $v_{1/2}$ is given by $X_{1/2}/t_{1/2}$. As explained, the increasing/decreasing intervals of relative humidities between 5% and 35% are of 10%, while those from 35% to 95% are of 20% of relative humidity. Then, rates of half absorption in the range 35-95% are twice than those in the range 5-35%. For comparative purposes the rates of the upper humidity range will be reduced by half yielding the corrected half sorption rate $v^*_{1/2}$. The existence of a water content gradient between the external surface and inside the specimen causes moisture to diffuse toward the centre of the specimen at a rate proportional to the gradient. If water content gradient is expressed in terms of weight of moisture per unit volume of substrate, the diffusion coefficient D will be

the amount of moisture diffusing in unit time across a unit area of the specimen under a unit gradient of adsorbable water. Thus, D will be a measure of both the diffusing properties of moisture and the permeability of the specimen. It is not easy to evaluate the volume and the external surface of a leather specimen. If we replace the volume by the mass of the specimen, the gradient of moisture concentration gradient is expressed in grams of adsorbable moisture per 100 g of dry specimen, resulting in an “apparent diffusion coefficient” D_A , which will be equal to the grams of moisture adsorbed in unit time by 100 g of dry specimen under a unit concentration gradient of adsorbable moisture, measured in min^{-1} , that is obtained using the Vickerstaff’s method [21] used to study the diffusion of dyes in fibres. Diffusion is well fitted by an expression derived from Fick’s equation that we apply in diffusion of moisture. This expression gives surprisingly satisfactory results in the early stages of moisture adsorption as in dye diffusion. If the fractional absorbed/desorbed moisture is plotted against the square root of the absorption/desorption time, the points lie on a straight line:

$$X(t) / X = \sqrt{D_A} \sqrt{t}$$

being the maximum slope the square root of the apparent diffusion coefficient D_A .

a) Regain $X(t)$ in % odw



b) Fractional regain

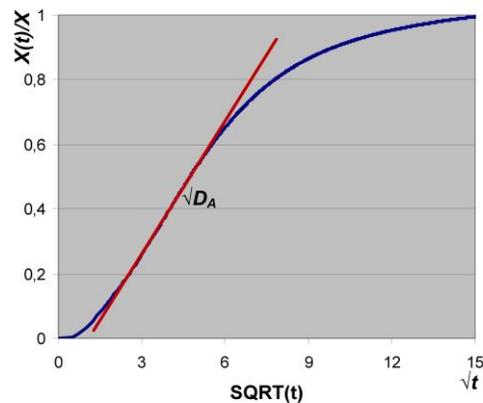


Figure 2 a) Mass increase in % odw caused by moisture absorption at one step along time, up to the equilibrium X . including values of half regain $X_{1/2}$ and half absorption time $t_{1/2}$; b) Fractional absorption $X(t)/X$ vs. square root of time. The maximum slope reflects the square root of the apparent diffusion coefficient D_A .

3 RESULTS AND DISCUSSION

Table 2 summarize the results of the parameters of fitted GAB model in absorption, the specific surface of absorption, mean values of hysteresis between 5 and 75% of relative humidity, the

apparent density and tearing energy of non fatliquored and fatliquored samples at the two steps (before finishing, i.e. in crust C, and after finishing F), according to the different fatliquors applied. Methods are explained elsewhere [22, 23].

Table 2: GAB model parameters in absorption (X_m , C , K), estimated maximum absorption capacity X_I at RH 100%, specific surface of absorption S , mean value of hysteresis between 5 and 75% of relative humidity H , apparent density D and tearing energy TE of the samples according to the fatliquor and step (C in crust and F finished) applied.

Fatliquor Step	No		TCSi/PGR		TCSi		PGR		ESF		PSi	
	C	F	C	F	C	F	C	F	C	F	C	F
X_m (%)	10,55	9,46	11,32	9,00	9,87	8,23	10,59	7,95	10,45	8,79	9,98	8,85
C	5,01	5,81	4,92	5,83	4,78	5,91	4,59	6,37	4,50	5,35	5,09	5,51
K	0,81	0,82	0,80	0,82	0,79	0,82	0,79	0,84	0,79	0,81	0,80	0,81
X_I (%)	52,59	51,10	49,18	47,46	43,62	43,33	47,73	47,88	46,9	44,35	46,86	45,84
S (m ² /g)	374,2	335,5	401,5	319,2	350,1	291,9	375,6	282,0	370,6	311,8	354,0	313,9
H (%)	69,0	64,7	65,3	61,8	62,1	62,2	62,2	67,7	60,2	60,7	59,3	61,5
D (g/cm ³)	0,621	0,650	0,588	0,649	0,640	0,689	0,637	0,678	0,632	0,653	0,656	0,699
TE (N/mm)	25,30	39,77	39,74	57,26	49,60	89,34	73,53	74,21	68,22	103,0	57,89	87,43

In order to analyze the kinetics of moisture absorption/desorption kinetics, the corrected rates of half absorption/desorption $v^{*1/2}$, the time elapsed to attain the maximum diffusion t_{max} yielded by the plot of the fractional absorption/desorption vs. the square root of time and the apparent diffusion coefficient given by the square of the slope DA at t_{max}

are considered. The results for non fatliquored leather and that fatliquored by the standard fatliquoring agent used as reference (TCSi/PGR) are shown in Table 3, those of their components TCSi and PGR in Table 4, and the results corresponding to ESF and PSi in Table 5.

Table 3: Results of corrected rates of half absorption/desorption $v^{*1/2}$, times for maximum diffusion t_{max} and apparent diffusion coefficients D_A , of non fatliquored leather *No* and that fatliquored by the *TCSi/PGR* combination in crust C and after finishing F. Absorbed and desorbed regains according to step are included.

Fatliquor Step	No				TCSi/PGR							
	$v^{*1/2} \times 10^2 (\%/min)$		$t_{max} (min)$		$D_A \times 10^2 (min^{-1})$		$v^{*1/2} \times 10^2 (\%/min)$		$t_{max} (min)$		$D_A \times 10^2 (min^{-1})$	
	C	F	C	F	C	F	C	F	C	F	C	F
<i>Absorption:</i>												
5→15%	11,25	11,32	7,58	7,75	3,18	3,36	13,56	9,02	6,25	9,00	4,10	2,89
15→25%	7,35	7,58	3,79	4,50	2,25	2,39	8,67	6,46	3,00	5,75	2,73	2,11
25→35%	5,68	5,88	3,16	2,50	1,74	1,94	6,53	5,24	1,75	4,75	2,20	1,72
35→55%	4,83	7,44	2,97	13,75	1,24	2,65	5,58	6,23	1,88	14,25	1,58	2,38
55→75%	5,33	7,22	34,04	16,25	1,06	1,90	6,26	5,87	25,38	20,00	1,24	1,57
75→95%	7,33	7,78	46,57	28,75	0,77	0,76	7,99	6,47	37,87	35,25	0,86	0,68
<i>Desorption:</i>												
95→75%	10,30	12,03	19,37	20,00	1,43	1,86	11,36	9,76	15,87	25,25	1,67	1,60
75→55%	8,27	9,91	8,38	11,00	1,77	2,39	9,47	8,11	7,25	12,50	2,19	2,08
55→35%	7,32	9,06	5,37	8,50	1,88	2,56	8,50	7,42	4,12	10,25	2,45	2,28
35→25%	7,43	7,34	4,50	4,50	2,02	2,24	8,72	6,33	3,50	5,25	2,53	2,04
25→15%	8,36	7,91	5,25	5,00	2,15	2,02	9,23	6,76	4,50	6,50	2,45	1,84
15→5%	9,39	8,73	14,49	13,25	1,72	1,67	9,91	7,40	8,25	17,25	1,92	1,56
<i>In crust: Regain absorbed (5 - 95%): 41,17%</i>						<i>In crust: Regain absorbed (5 - 95%): 38,85%</i>						
<i>Regain desorbed (95 - 5%): 38,55%</i>						<i>Regain desorbed (95 - 5%): 36,33%</i>						
<i>Finished: Regain absorbed (5 - 95%): 39,44%</i>						<i>Finished: Regain absorbed (5 - 95%): 36,81%</i>						
<i>Regain desorbed (95 - 5%): 37,03%</i>						<i>Regain desorbed (95 - 5%): 34,61%</i>						

Table 4: Results of corrected rates of half absorption/desorption $v^{*}_{1/2}$, times for maximum diffusion t_{max} and apparent diffusion coefficients D_A , of leathers fatliquored with **TCSi** and **PGR** in crust C and after finishing F. Absorbed and desorbed regains according to step are included.

Fatliquor Parameter Step	TCSi				PGR							
	$v^{*}_{1/2} \times 10^2 (\%/min)$		$t_{max} (min)$		$D_A \times 10^2 (min^{-1})$		$V^{*}_{1/2} \times 10^2 (\%/min)$		$t_{max} (min)$		$D_A \times 10^2 (min^{-1})$	
	C	F	C	F	C	F	C	F	C	F	C	F
Absorption:												
5→15%	11,19	12,45	7,50	5,75	3,61	4,32	11,08	9,95	8,08	8,33	3,40	3,23
15→25%	7,79	8,58	4,00	2,50	2,72	3,36	7,79	7,30	5,00	4,58	2,58	2,87
25→35%	6,03	6,48	2,67	2,08	2,21	2,80	5,93	5,86	3,00	3,50	2,16	2,65
35→55%	7,47	8,17	13,08	10,13	2,55	3,09	7,14	6,26	12,63	12,58	2,22	2,26
55→75%	7,81	8,19	14,78	12,17	2,34	2,63	7,56	6,17	16,67	15,92	1,99	1,79
75→95%	7,34	8,17	25,17	22,79	0,82	0,91	7,31	6,51	27,42	34,67	0,76	0,65
Desorption:												
95→75%	11,58	13,37	20,00	16,25	2,09	2,35	11,34	10,33	20,83	23,17	1,83	1,72
75→55%	9,74	10,70	9,58	8,50	2,73	3,05	9,63	8,53	11,67	12,13	2,46	2,30
55→35%	8,90	9,65	6,92	7,13	2,91	3,38	8,77	7,76	9,08	9,42	2,65	2,49
35→25%	7,36	8,18	4,17	3,83	2,52	3,20	7,36	6,71	4,67	4,08	2,29	2,28
25→15%	7,72	8,61	5,00	4,38	2,18	2,62	7,81	7,08	6,42	7,92	2,01	1,93
15→5%	8,33	9,55	14,58	9,58	1,72	2,04	8,68	7,75	14,00	16,33	1,65	1,57
In crust: Regain absorbed (5 - 95%): 34,99%						In crust: Regain absorbed (5 - 95%): 38,13%						
Regain desorbed (95 - 5%): 32,91%						Regain desorbed (95 - 5%): 35,98%						
Finished: Regain absorbed (5 - 95%): 33,78%						Finished: Regain absorbed (5 - 95%): 36,21%						
Regain desorbed (95 - 5%): 31,85%						Regain desorbed (95 - 5%): 34,15%						

The application of the ANOVA to the experimental results enabled us to estimate the effect of fatliquoring agent, step (crust, finished), mode (absorption, desorption) and relative humidity on the diffusion parameters (rate of half absorption corrected to a gradient of 10%

RH $v^{*}_{1/2}$, time for maximum diffusion t_{max} and apparent coefficient of diffusion D_A), which explain the easiness of moisture interchange between leather and environment. Table 6 summarizes the signification of the effects and interactions.

Table 5: Results of corrected rates of half absorption/desorption $v^{*}_{1/2}$, times for maximum diffusion t_{max} and apparent diffusion coefficients D_A , of leathers fatliquored with **ESF** and **PSi** in crust C and after finishing F. Absorbed and desorbed regains according to step are included.

Fatliquor Parameter Step	ESF				PSi							
	$r^{*}_{1/2} \times 10^2 (\%/min)$		$t_{max} (min)$		$D_A \times 10^2 (min^{-1})$		$R^{*}_{1/2} \times 10^2 (\%/min)$		$t_{max} (min)$		$D_A \times 10^2 (min^{-1})$	
	C	F	C	F	C	F	C	F	C	F	C	F
Absorption:												
5→15%	12,19	10,64	6,75	7,75	3,81	3,62	12,04	12,05	6,00	6,00	3,43	4,08
15→25%	7,99	7,51	2,75	4,25	2,67	2,71	5,35	8,14	2,00	2,75	2,56	2,95
25→35%	6,25	6,07	2,50	3,50	2,07	2,29	3,56	6,34	1,50	2,25	1,99	2,27
35→55%	7,98	7,11	13,00	10,50	2,68	2,63	6,70	7,89	15,50	11,50	2,29	3,00
55→75%	8,02	7,09	16,00	16,00	2,10	1,99	8,20	7,41	16,50	14,75	2,18	2,04
75→95%	7,78	7,42	25,75	26,50	0,83	0,83	7,88	7,69	26,25	28,50	0,84	0,83
Desorption:												
95→75%	11,83	11,53	20,50	19,75	1,91	1,96	12,22	11,72	18,25	20,75	1,95	1,98
75→55%	10,14	9,59	11,25	10,00	2,63	2,62	10,49	9,97	10,25	11,00	2,74	2,70
55→35%	9,64	8,87	8,50	8,00	2,92	2,93	9,74	9,34	7,25	8,00	3,00	3,00
35→25%	8,04	7,46	4,25	4,50	2,59	2,59	8,22	7,88	3,75	4,00	2,74	2,74
25→15%	8,68	7,81	5,25	5,25	2,33	2,30	8,95	9,14	5,00	4,75	2,43	2,45
15→5%	9,78	8,59	10,00	10,00	1,99	1,90	10,06	9,73	9,50	10,75	2,07	2,09
In crust: Regain absorbed (5 - 95%): 37,38%						In crust: Regain absorbed (5 - 95%): 37,11%						
Regain desorbed (95 - 5%): 35,16%						Regain desorbed (95 - 5%): 34,81%						
Finished: Regain absorbed (5 - 95%): 34,67%						Finished: Regain absorbed (5 - 95%): 35,66%						
Regain desorbed (95 - 5%): 32,62%						Regain desorbed (95 - 5%): 33,32%						

Table 6: Summary of the signification of **Fatliquor**, **Step** (crust, finishing), **Mode** (absorption, desorption), **Relative Humidity** and their interactions (**FxS**, **FxM**, **FxRH**, **SxM**, **SxRH**, **MxRH**) on diffusion parameters: rate of half absorption $v^{*1/2}$, time for maximum diffusion t_{max} and apparent diffusion coefficient D_A .

Diffusion parameters	Main effects					Interactions				
	Fatliquor	Step	Mode	RH	FxS	FxM	FxRH	SxM	SxRH	MxRH
$v^{*1/2}$	0,0%	2,5%	0,0%	0,0%	0,0%	n.s.	n.s.	n.s.	5,0%	0,0%
t_{max}	1,0%	n.s.	0,0%	0,0%	5,0%	n.s.	n.s.	n.s.	n.s.	0,0%
D_A	0,0%	0,1%	n.s.	0,0%	0,0%	n.s.	n.s.	n.s.	5,0%	0,0%

Note: n.s. – non-significant effect.

As shown in Table 6 diffusion parameters are significantly influenced by fatliquor, step (crust, finished), mode (absorption, desorption) and relative humidity and the interactions between fatliquor and step, and between relative humidity and both step and mode. Consequently discussion will be based on interaction plots in which the effect of all factors can be assessed. Figure 3 shows the effect of relative humidity and step in diffusion parameters. Regardless fatliquoring it can be observed that the initial half sorption rate decreases up to 30% RH but when exceeded turns to ascend. At 10% RH initial sorption rate is higher in crust than in finished samples which can be related with their higher size of the monolayer. Moisture initially absorbed by leather hinders the entrance of subsequent moisture decreasing the initial rate up to 30%RH but the increase

in partial pressure of moisture by the increase in relative humidity balances hindering and makes the initial rate to increase with partial pressure or relative humidity. From 20% of RH no significant differences in the initial diffusion rate between crust and finished are observed. No differences between crust and finished samples are observed as regards the time to attain the steady diffusion regime than decreases up to 30% RH and then turns to ascend probably due to the fact that moisture is placed in the inner parts of the sample. As regards the apparent coefficient of diffusion, finishing favours diffusion especially for relative humidities around 45%. At higher RH secondary water is placed in multilayers: this explains the decrease of the coefficients and the growth in time for maximum diffusion.

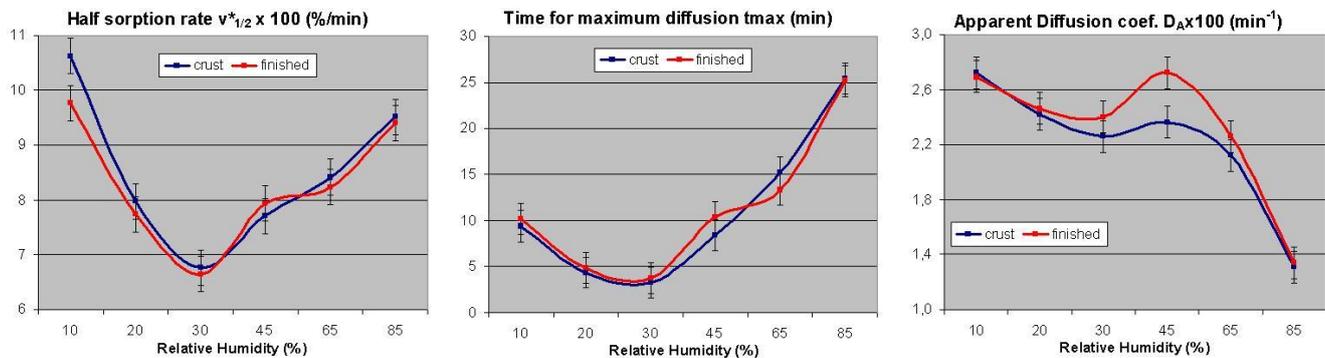


Figure 3 Effect of the relative humidity and step (crust, finishing) on diffusion parameters (corrected half sorption rate, time for maximum diffusion and apparent diffusion coefficient).

Figure 4 shows the effect of relative humidity and mode in diffusion parameters. It appears that the initial rate of sorption is higher in desorption than in absorption except when primary water strongly linked to leather at lower RH is involved [24]. As regards the time for maximum diffusion (to reach the steady state) variation in desorption are more balanced than that in absorption

being longer at lower RH and shorter in higher RH. Similar evolution is observed in relation with the diffusion coefficient. Variation in desorption is more balanced than that in absorption. The diffusion of primary strongly linked water can be observed at lower RH, that of the secondary weakly linked one at medium values of RH, and the diffusion of free water at the higher RH levels.

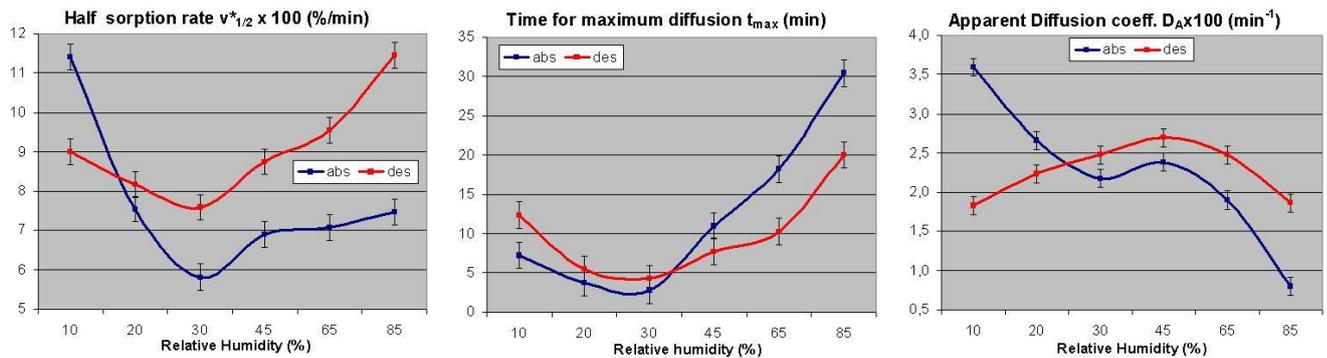


Figure 4 Effect of the relative humidity and mode (absorption, desorption) on diffusion parameters (half sorption rate, time for maximum diffusion and apparent diffusion coefficient).

Figure 5 shows that the effect of finishing on diffusion parameters depends on the fatliquor used. Finishing in non fatliquored

leather makes the initial diffusion rate to ascend, reaching faster the steady (lower t_{max}) and increasing the diffusion coefficient.

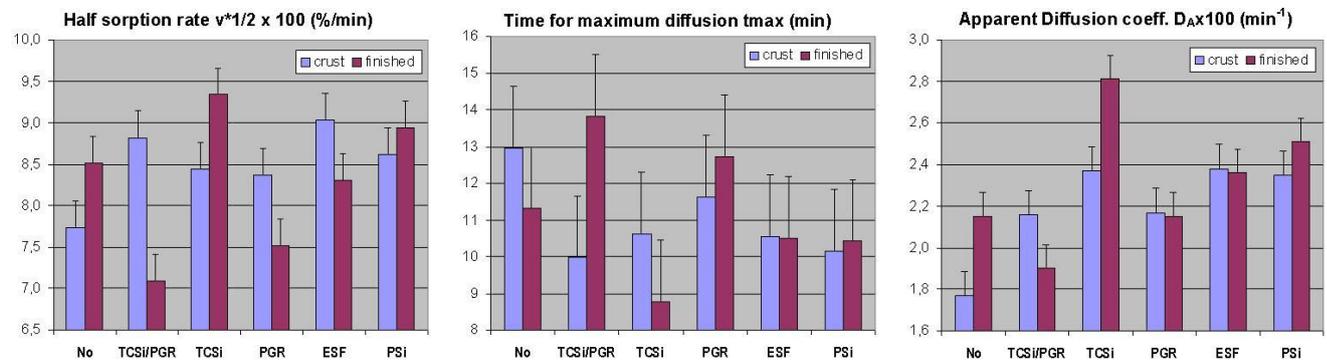


Figure 5 Effect of fatliquor and step (crust, finishing) on diffusion parameters (half sorption rate, time for maximum diffusion and apparent diffusion coefficient)

Similar effects of finishing can be observed when leather is fatliquored with TCSi although it shows the highest initial rates, the lowest times for steady diffusion and the greatest diffusion coefficients. As regards leather finished with standard mixture (TCSi/PGR) finishing causes the opposite effects: a strong decrease in the initial rate a significant ascend in time for maximum diffusion and a decrease in the diffusion coefficient. These seem to be the expected effects of finishing taking into account that this operation causes an increase in the apparent density of leather. When leather is fatliquored with the other component of the mixture, PGR the effects, although are shorter, show the same tendencies for the initial rate and the time for maximum diffusion. The diffusion coefficient after finishing remains the same. When we consider leathers fatliquored with ESF and PSi no significant effects of finishing are

observed in the time for maximum diffusion and the diffusion coefficient, although significantly decreases the initial diffusion rate of ESF while the initial rate for PSi is non significantly modified.

As regards the diffusion parameters no differences between crust and finished steps are observed in non fatliquored leather at low relative humidities up to 30%. Focussing on the apparent coefficient of diffusion a continuous decrease with relative humidity can be observed in non fatliquored sample and that fatliquored with standard fatliquoring in crust state. But, after finishing and with the other fatliquors regardless the step, the evolution of the diffusion coefficient with the relative humidity is similar to that shown in Figure 4.

Boulton, Reading and Neale studied the relationship between the rate of dyeing and diffusion inside the fibre and the results are explained by Vickerstaff [21]. As regards the

diffusion of direct dyes on viscose rayon, these authors plotted the apparent diffusion coefficients against the half-times of dyeing in logarithmic basis. According to them, all points lie close to a straight line whenever the rate of dyeing is determined by the rate of diffusion inside the fibre. We applied the same criteria to evaluate the rate of moisture absorption/desorption and the diffusion inside all leather treated samples. Figure 6a confirms the linear relationship between the logarithms of the apparent diffusion

coefficient and the time of half sorption. A deeper examination of the relationship between half adsorption time and the apparent diffusion coefficient suggests another linear relationship that is closer and more simple, [25] i. e. the regression between the inverse of the half time of sorption and the apparent diffusion coefficient, yielding the equation shown in Figure 6b, $DA = 0,437/t^{1/2}$ with a correlation coefficient of 0,996. Prediction intervals at 95% are included.

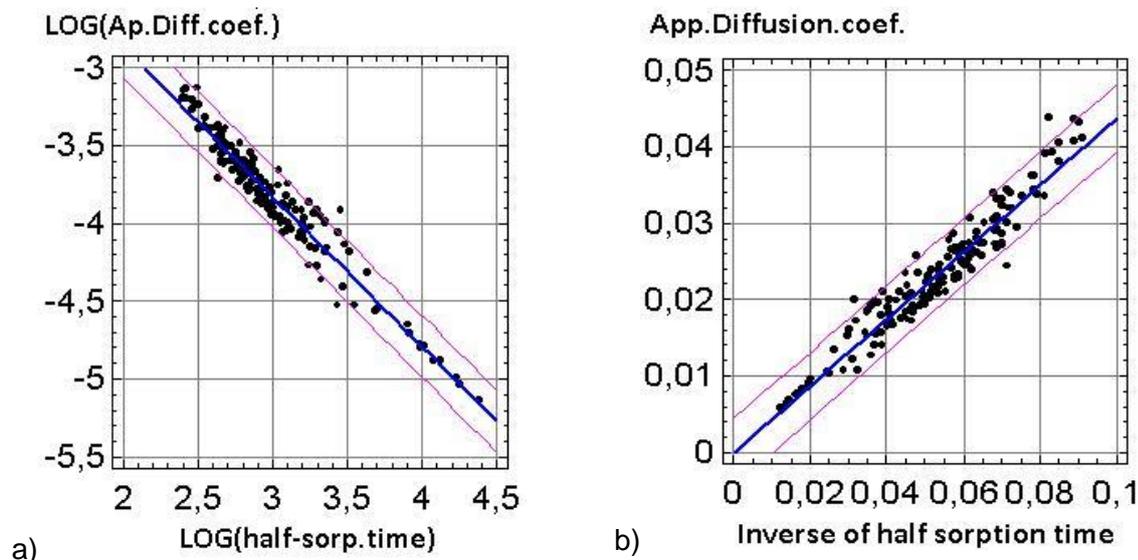


Figure 6 Linear relationships between a) the logarithms of the apparent diffusion coefficient and the half of sorption time, and b) that of the apparent diffusion coefficient and the inverse of half-sorption time.

4 CONCLUSIONS

In the light of our findings, the following conclusions may be drawn:

- Diffusion parameters explain the kinetics of sorption that is independent of sorption results reached at the equilibrium.
- Diffusion parameters are significantly influenced by fatliquor, step (crust, finished), mode (absorption/desorption) and relative humidity.
- The initial half-sorption rate tends to decrease up to 30% RH and then, tends to ascend. At lower relative humidities crust samples show higher initial rates than finished ones, and the diffusion coefficient of finished samples is higher than crust ones when RH is around 45%.
- As regards the time for maximum diffusion that shows a minimum at 30% RH, no differences are observed

- between crust and finished samples.
- When mode of sorption is considered, higher half-sorption rates and diffusion coefficients are observed at lower relative humidities, while the contrary occurs at higher relative humidities.
- The evolution of the apparent diffusion coefficient of all crust and finished samples follows the plot shown in Figure 4, except for crust samples non fatliquored and fatliquored with TCSi/PGR which progressively decrease as relative humidity increases.
- The linear relationship between the logarithmic form of the time of half adsorption and the apparent diffusion coefficient suggests that the rate of adsorption is governed by the diffusion of moisture inside the sample.

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5 REFERENCES

1. Bajza Z., Vrcek I.V.: *J Mater Sci* 36, 5265-5270, 2001
2. Mitton R.G.: *J Soc Leath Tech Ch*, 54, 248-266, 1970
3. Komanowsky M.: *J Am Leather Chem As*, 86, 269-280, 1989
4. Tuckerman M., Mertig M., Pompe W., Reich G.: *J Mater Sci* 36, 1789-1799, 2001
5. Bienkiewicz K.: "Physical Chemistry of Leather Making", RE Kriger Publishing Company, Malabar, Florida, 1983, p. 110
6. Bosch T, Manich A.M., Carilla J., Cot J., Marsal A., Kellert H.J., Germann H.P.: *J Am Leather Chem As* 97, 441-450, 2000
7. Hole L.G.: *J Soc Cosmet Chem*, 24, 43-63, 1973
8. Svennberg K., Lengsfeld K., Hardekup L.E., Holm A.: *J Build Phys*, 30, 3, 261-274, 2007
9. Dernovšková J., Jirasová H., Zelinger J.: *Restaurator*, 16, 31-44, 1995
10. Pineri M.H., Escoubes, M., Roche, G.: *Biopolymers*, 17, 2799-2815, 1978
11. Grigera J.R., Berendsen H.J.C.: *Biopolymers*, 18, 47-57, 1979
12. Caurie M.: *Int J Food Sci Tech*, 40, 283-293, 2005
13. Timmermann, E.O.: *Colloid Surface A*, 220, 235-260, 2003
14. Dent R.W.: *Text. Res. J.*, 47, 145-152, 1977
15. Al-Muhtaseb A.H., McMinn W.A.M., Magee T.R.A.: *J Food Eng*, 61, 297-307, 2004
16. Kneule F.: "Enciclopedia de la Tecnología Química. Tomo I: El Secado", Ed. Urmo, S. A., Bilbao (Spain), pages 32-33, 1976
17. Palop R., Manich A.M., Marsal A.: *J Am Leather Chem As*, 102, 5, 145-153, 2007
18. Palop R., Manich A.M., Marsal A.: *J Am Leather Chem As*, 101, 11, 399-407, 2006
19. Higgins R A: "Properties of engineering materials", Edward Arnold, London, 1991
20. Otunga M.G.: "Effect of drying under strain on the mechanical properties of leather", PhD Thesis, University of Leicester, UK, 2002
21. Vickerstaff T.: "The Physical Chemistry of Dyeing", Oliver and Boid, London, 1954
22. Manich A.M., Barenys J., Martínez L., Lloria J., Carilla J., Marsal, A.: "Efecto del engrase en las características de confort de la piel. Parte III: Absorción y desorción de humedad", Proceedings 64 AQEIC Congress, Barcelona, 2016 (in Spanish)
23. Manich A.M., Barenys J., Martínez L., Lloria J., Marsal A.: *J Am Leather Chem As*, (in press) April 2016
24. Ussman M., López-Santana D., Carilla J., Manich A.M.: "Cellulosic Fibres and Water Sorption Isotherms", 10th Mediterranean Conference on Calorimetry and Thermal Analysis MEDICTA 2011, Proceedings, Porto, 2011
25. Manich A.M., Maldonado F., Carilla J., Catalina M., Marsal A.: *J Soc Leath Tech Chem*, 94, 1, 15-20, 2010

