

Effect of Fatliquoring on Leather Comfort. Part III: Moisture Absorption-Desorption of Leather

by

A.M. Manich,^{1*} J. Barenys,² L. Martínez,² J. Lloria,¹ J. Carilla¹ and A. Marsal¹¹*IQAC-CSIC, Department of Chemical and Surfactants Technology*

Jordi Girona, 18-26- 08034 Barcelona, Spain

²*Trumpler Española S.A.*

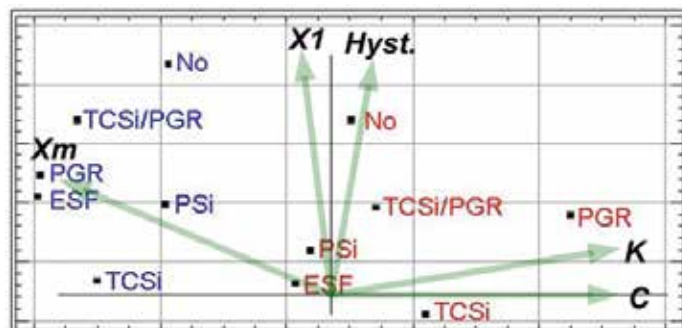
Carrer Llobateres 15, 08210 Barberà del Vallès, Spain

Abstract

The comfort of tanned hide/skin is an added value, which is decisive for the choice of leather in articles for footwear or clothing, compared to other alternatives whose design excludes this component. This comfort is related to the capacity of absorption and desorption of moisture and with the physical, mechanical and organoleptic characteristics of the leather. After tanning, fatliquoring and retanning are the operations that more intensively modify the characteristics of leather articles.

This work is a continuation of two previous ones that have studied the influence of fatliquoring on softness and compressibility of leather and on grain and corium quality of leather assessed by ball bursting and tearing tests. In this case, the effect of fatliquoring on moisture absorption-desorption characteristics of leather is studied. The experimental work has been carried out in the pilot plant of Trumpler Española S. A. and the moisture absorption-desorption tests in the Laboratory of Thermal Analysis and Calorimetry of the IQAC. The behavior of non-fatliquored leather and that of leather fatliquored with a combination of sulphited triglycerides of colza oil and fatty polymer (TCSi/PGR) or fatliquored separately with their components TCSi and PGR, or with phosphoric ester ESF or sulphited fish oil Psi has been determined.

The determination of the size of the moisture absorbing monolayer (X_m), the binding energy constants of the monolayer C and the multilayer K, the maximum absorption capacity at saturation X_1 and the hysteresis (Hyst.) between absorption and desorption, enabled us to classify the different fatliquoring agents according to stage (crust-blue, finished-red) by applying factorial analysis (see following graph). Finishing is the factor that best explains this behavior. Finishing decreases the size of the monolayer and increases the binding energy constants. Fatliquoring decreases the maximum absorption capacity and hysteresis, partially affecting the reduction of the monolayer size.



Introduction

The comfort of tanned hide/skin is an added value, which is decisive for the choice of leather in articles for footwear or clothing, compared to other alternatives whose design excludes this component. This comfort is related to the capacity of absorption and desorption of moisture¹ and with the physical, mechanical and organoleptic characteristics of the leather.² After tanning, fatliquoring and retanning are the operations that more intensively modify the characteristics of leather.^{3,4} This work is a continuation of two previous ones in which the influence of fatliquoring on the softness and compressibility of leather⁵ and on the resistance to grain cracking and to tearing load⁶ have been studied.

When leather is used as component in footwear or garment, the relative humidity of its environment depends on the user conditions, causing vapor diffusion phenomena between leather and the environment to recover the dynamic balance between both. If external relative humidity grows, water molecules are accumulated to the outer surface of leather; then are gradually diffused inwards, thanks to the concentration gradient existing between outer and inner parts up to the equilibrium is reached.

The water absorption capacity of collagen is explained by its fibrous structure and the high content of hydrophilic groups of this protein. In a study on the water-collagen interaction carried out with animal

*Corresponding author e-mail: albert.manich@iqac.csic.es

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tendons, Pineri⁷ described the different mechanisms of water fixation. Grigera⁸ distinguished two types of water: one bound to the macromolecular structure of collagen in definite positions by means of hydrogen bonds and, the other, which slightly interacts with water already bound to the macromolecule, forming multilayer with similar properties of that of water in liquid state. This view agrees with that of Caurie,⁹ who describes three types of water: a) *primary water*, which is absorbed by the most energetic groups -strongly bound water-, b) *secondary water* consisting of water molecules, which are slightly bound to the former and c) *free water*, which condensates at saturation pressure. The water content can be described as *regain* when referred to the mass of dry matter or *humidity* when referred to the total mass, including water.

Absorption Isotherms

The classic Brunauer, Emmett and Teller (BET) absorption model is based on the good correlation between the number of water molecules linked to the first absorption layer and the number of polar groups of the absorbent. It is assumed that each polar group links one water molecule, which, in turn, can capture other molecules diffusing to the interior of the material thanks to the increase of relative humidity (water activity) of the exterior. BET equation is used to calculate the size of the monolayer of the most diverse materials and is recognized by the IUPAC for the calculation of the specific surface of absorption. In 1985, the Colloid and Surface Chemistry Commission recommended BET equation to estimate monolayer size at relative humidity between 5 and 30%, i.e., water activities between 0.05 and 0.30.

The Guggenheim, Anderson and de Boer (GAB) model also estimates the monolayer size and shows a higher application since the range of relative humidity/water activity is much wider (between 0.05 and 0.8-0.9)¹⁰. BET and GAB isotherms are based on the same hypothesis and share the following parameters: size of the monolayer X_m and the energy constant of it C . The GAB model introduces a second energy constant for the multilayer, K . Both constants determine the plot shape of water content in the material with water activity. The first constant, C , defines the initial convexity at low relative humidity and is proportional to the variation of the ratio between absorption and desorption rates when the partial pressure of humidity for the monolayer changes⁽¹⁰⁾. The K constant defines the concave shape at high values of relative humidity. It depends on the ratio between the absorption and desorption rates of the water molecules placed in the upper layers. The lower the value of K , the less structured the multilayer of sorbate in relation with the pure liquid state. K increases with stronger interactions between sorbate and sorbent.¹⁰

The isotherm shape depends on how the sorbate is bound to the sorbent. When the absorption and desorption isotherms are not coincident, it is said that there is hysteresis in the process and its extent is related with composition and characteristics of the material, accessibility of water molecules to the most energetic polar groups of

the interior¹¹ and the ease of redistribution and rearrangement of the sorbate into the sorbent. The absorption isotherms for collagen are of Type II and III: at low relative humidity a moderate absorption of water occurs while at high humidity a considerable growth in absorption is done.¹² Table I shows the parameters of BET and GAB models that define the isotherm shapes.^{13,14}

Fatliquoring agents penetrate the inside of hide and act as lubricant between collagen micro fibrils improving handle and making ease the relative displacement of micro fibrils when subjected to mechanical stresses; logically, its presence also modifies its characteristics of humidity absorption and desorption.

Objective

The aim of this work is to study the influence of both finishing and fatliquoring on the characteristics of humidity absorption and

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

Model	Mathematical equation
BET ¹³ GAB ¹⁴	$X = X_m C a_w / [(1-a_w)(1-a_w + C a_w)]$ $X = X_m C K a_w / [(1- K a_w)(1- K a_w + C K a_w)]$
Parameter	Definition
a_w	Water activity expressed as vapor relative pressure p/p_0 , where p_0 is the vapor pressure at saturation
X	Equilibrium moisture content at a_w in g of absorbed water / 100 g of sorbent on dry basis
X_m	Monolayer moisture content in g of absorbed water / 100 g of sorbent on dry basis (d.b.)
C	Energy constant related to the difference between the free enthalpy of water molecules in the pure liquid state and in the monolayer. This is proportional to the rate between both the attachment and the escape rates for the primary sites
K	Ratio between the standard vapor pressure of the liquid and the vapor pressure of the sorbate in the secondary (upper) layers. Proportional to the rate between the attachment rate and the escape rate for all higher layers.

desorption of leather. Humidity absorption/desorption isotherms at 25°C between 5 and 95% of relative humidity will be determined. The size of the monolayer, the energy constants of monolayer and multilayer, the maximum absorption capacity at saturation and the hysteresis before and after finishing will be determined, in order to evaluate the effect of fatliquoring agent and finishing on these parameters. Existing relationships between structural parameters of leather are also explored.

Materials

Wet-blue sides from Ireland, shaved to a thickness of 1.2-1.4 mm were used as the starting material. The processing of the sides was carried out at the pilot plant of Trumpler Española S.A. 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 provided by the same company. To compare the effect of the fatliquoring agents on the absorption/desorption models, one of the sides was not fatliquored. Fatliquoring was carried out by applying a 7% of active matter on shaved weight. After a final washing, a light standard finishing was applied to one half of each leather sample to determine the possible effect of the finishing operation on humidity absorption/desorption parameters.

Fatliquors were identified by their main characteristic component:

- Sulphited triglycerides of rapeseed oil, *TCSi*
- Fatty Polymers (non-waterproofing), *PGR*
- Phosphoric Ester, *ESF*
- Sulphited fish oil, *PSi*
- The combination (*TCSi/PGR*), which was used as reference

Methods

Moisture absorption/desorption isotherms of samples of approximately 12 mg have been obtained by the Q5000SA Dynamic Vapor Sorption DVS Analyzer (TA Instruments) using the following procedure:

1. Initial drying at 60°C and 0% of relative humidity for 1 hour
2. Pre-stabilization at 25° and 0% of relative humidity and, then, the sample is subjected to a relative humidity of 5% up to stabilization

3. Absorption stages: the sample previously stabilized at 5% of relative humidity is subjected to absorption stages that progressively increases from 15% to 25%, 35%, 55% 75% and 95% of relative humidity.
4. Desorption stages: the sample stabilized at 95% relative humidity is subjected to decreasing desorption stages from 75% to 55%, 35%, 25%, 15% and 5% of relative humidity.
5. Final stage conditions: to shorten the duration of the stages, each stage lasts a maximum of 500 min. However, if variation in weight is less than 0,02% for 10 min., the stage is considered to be finished because quasi-equilibrium conditions have been reached.

The software of TA Instruments provides the BET and GAB model parameters of the absorption isotherm for the final humidity

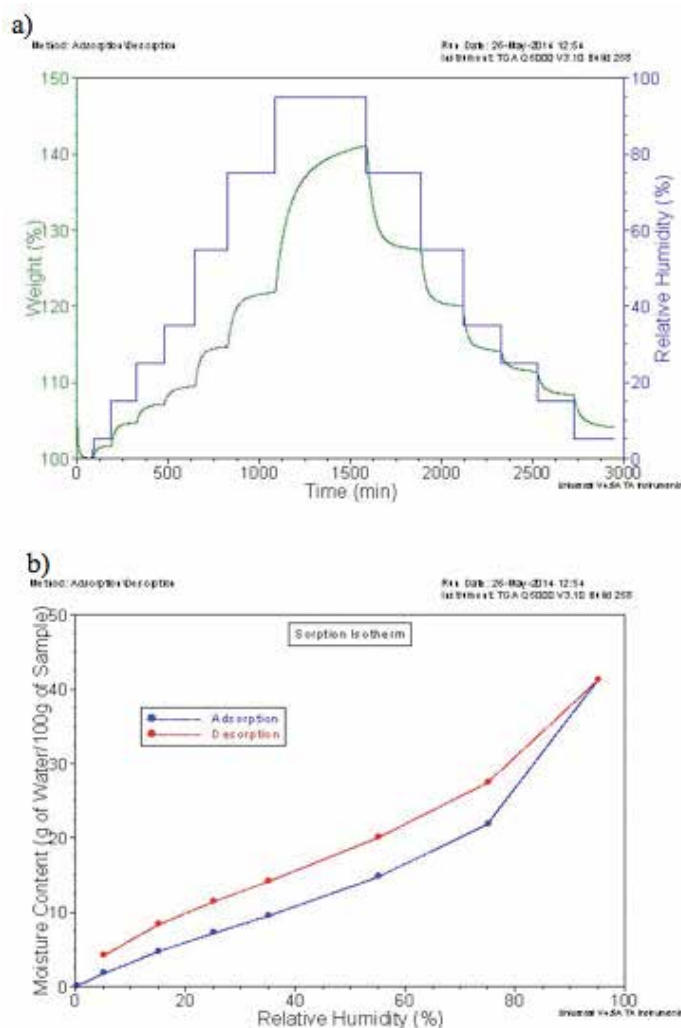


Figure 1. a) Variation of sample mass (%) with time in function of the relative humidity steps in absorption and desorption according to the measuring procedure; b) Absorption/desorption isotherm plot connecting the quasi equilibrium conditions at the end of each step of absorption and desorption.

content of each stage. Figure 1 shows the results obtained during the absorption and desorption tests and the resulting isotherm.

Table II shows the results of “regain” (moisture % referred to mass of dry sample) at the end of each stage of absorption and desorption, when the quasi-equilibrium conditions have been reached. These results are for the non-fatliquored sample as well as for samples treated with the five fatliquoring agents (*TCSi/PGR*, *TCSi*, *PGR*, *ESF* and *PSi*), before(C) and after (F) finishing.

Calculation of Absorption and Desorption Isotherms

The software of the thermo balance provides the GAB parameters to the absorption isotherm, which are used as initial estimators for obtaining the absorption isotherm parameters by applying an iterative non-linear regression procedure, which also allows to obtain the equation of the desorption isotherm¹⁵. The GAB model in absorption allows estimating the absorption of the sample at saturation ($a_w = 1$), i.e., the maximum moisture absorption capacity of the sample (X_1), provided that (K) is less than 1. In order to fit the GAB model to the desorption isotherm, the maximum absorption capacity (X1) is considered instead of that corresponding to 95% of relative humidity, since it would not correspond to the value reached

in desorption. Figure 2 shows the absorption and desorption isotherms for crust and finished leather. The parameters of GAB model in absorption, desorption and the maximum absorption capacity (X_1) are shown in Table 3.

Specific Surface of Absorption

The absorption specific surface (S in m²/g) is calculated by applying the equation $S = 0.01 X_m L n / M$,¹⁶ where L is the surface covered by one water molecule (10.6 x 10⁻²⁰ m²), M is the molecular mass of water (18 g/mol) and n is the Avogadro’s number (6.022 x 10²³).

Hysteresis

The hysteresis between absorption and desorption isotherms, reflects structural changes occurring in the material due to the interaction with absorbed water. Hysteresis is determined at each level of water activity or relative humidity by applying the following equation:

$$\text{Hysteresis (\%)} = 100 \times (X_d - X_a) / X_d$$

where X_d is the water content in desorption and X_a is the water content in absorption in the quasi-equilibrium conditions at each level of humidity, expressed as % of water on dry mass of fiber. If

Table II

Regain (moisture content of samples in % of water referred to dry mass) at the end of each stage in absorption and desorption in function of the different fatliquoring agents, before C (in “crust”) and after F finishing at different levels of relative humidity or water activity a_w (=RH%/100). Fatliquoring agents: TCSi Sulphited triglycerides of rapeseed oil, PGR Fatty Polymers (non-waterproofing), ESF Phosphoric Ester, PSi Sulphited fish oil and the combination TCSi/PGR used as reference.

RH/100	<i>Non fatliq'd</i>		<i>TCSi/PGR</i>		<i>TCSi</i>		<i>PGR</i>		<i>ESF</i>		<i>PSi</i>	
	C	F	C	F	C	F	C	F	C	F	C	F
<i>In absorption:</i>												
0,05	1,74	1,71	1,64	1,63	1,44	1,36	1,53	1,47	1,60	1,50	1,61	1,56
0,15	4,84	4,71	4,63	4,47	4,31	4,12	4,59	4,30	4,46	4,21	4,68	4,27
0,25	7,37	7,14	7,10	6,80	6,59	6,23	7,00	6,38	6,78	6,35	6,93	6,47
0,35	9,87	9,49	9,52	9,04	8,79	8,27	9,27	8,27	9,13	8,42	9,19	8,66
0,55	15,48	14,70	14,93	13,84	14,12	13,00	14,96	12,86	14,63	13,11	14,48	13,47
0,75	23,48	21,85	22,48	20,65	20,60	18,64	22,34	19,25	22,01	19,77	21,70	20,06
0,95	42,93	41,16	40,50	38,43	36,43	35,14	39,66	37,68	38,98	36,17	38,72	37,22
<i>In desorption:</i>												
0,75	29,12	27,44	27,23	25,69	24,58	23,25	26,62	24,80	25,85	23,95	25,52	24,56
0,55	21,37	20,00	19,92	18,67	18,11	16,94	19,50	18,09	18,85	17,43	18,70	17,88
0,35	15,08	14,12	14,10	13,18	12,92	12,08	13,82	12,87	13,25	12,28	13,24	12,65
0,25	12,06	11,40	11,26	10,65	10,43	9,80	11,12	10,43	10,68	9,90	10,73	10,20
0,15	8,93	8,31	8,21	7,78	7,54	7,10	8,01	7,54	7,73	7,20	7,83	7,42
0,05	4,37	4,12	4,15	3,82	3,52	3,29	3,68	3,53	3,81	3,55	3,90	3,67

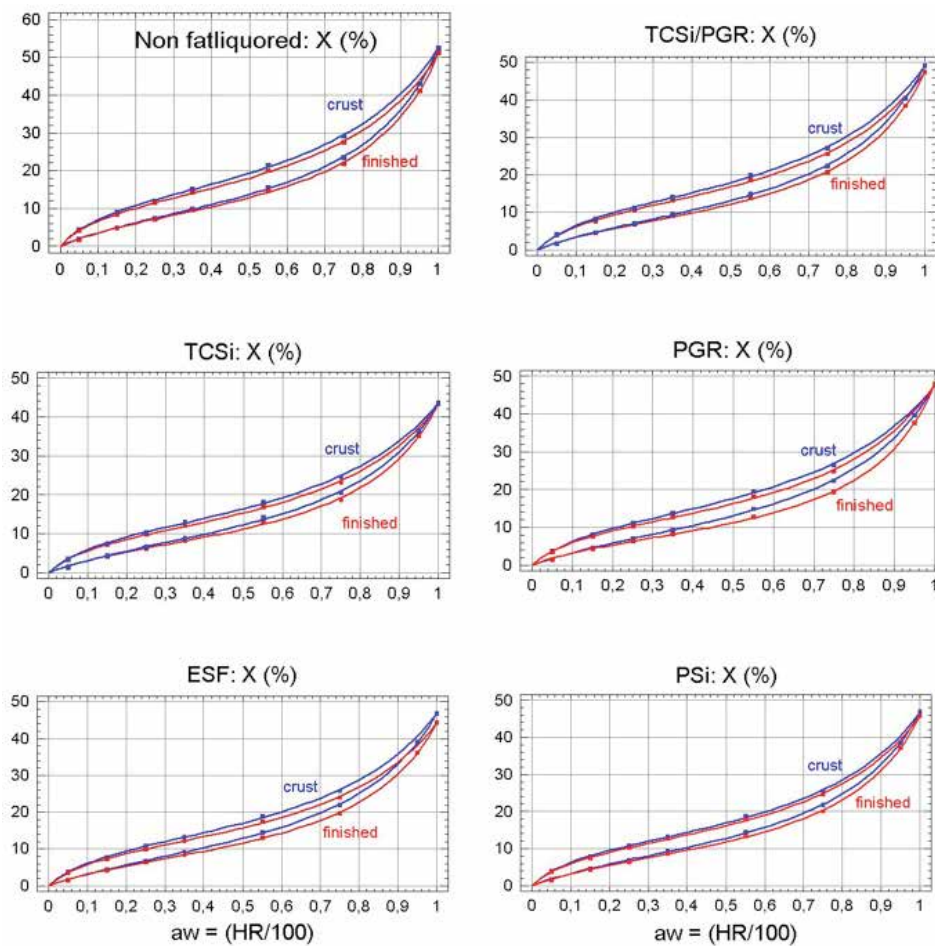


Figure 2. GAB fitted absorption and desorption isotherm of non fatliquored leather and those fatliquored with different fatliquoring agents before (blue plot) and after (red plot) finishing. Fatliquoring agents: TCSi Sulphited triglycerides of rapeseed oil, PGR Fatty Polymers (non waterproofing), ESF Phosphoric Ester, PSi Sulphited fish oil and the combination TCSi/PGR used as reference.

Table III

Results of the nonlinear fits of GAB model to the absorption isotherms (X_m , C and K), estimation of the maximum absorption capacity at saturation X_1 and those of desorption (X_{md} , C_d and K_d) as a function of the fatliquoring agent (see references in Table 2) before (C) and after (F) finishing.

Fitted results	Non fatliq'd		TCSi/PGR		TCSi		PGR		ESF		PSi	
	C	F	C	F	C	F	C	F	C	F	C	F
In absorption:												
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_1 (%)	52,59	51,10	49,18	47,46	43,62	43,33	47,73	47,88	46,9	44,35	46,86	45,84
In desorption:												
X_{md} (%)	10,09	12,92	13,16	12,16	12,17	11,00	13,10	11,46	12,47	11,34	12,14	11,55
C_d	10,67	11,02	10,59	10,83	10,43	10,94	9,98	11,32	10,31	10,70	11,21	11,00
K_d	0,74	0,75	0,74	0,75	0,73	0,75	0,74	0,77	0,74	0,75	0,75	0,76

hysteresis is plotted as a function of the relative humidity (RH), it can be observed that hysteresis decreases as RH increases. It is observed that hysteresis grows with the intensity at which water is attached to the material. When the first water molecules are incorporated into a hydrophilic material in dry state, they are directly linked to the reactive groups of the material, constituting the first absorption layer with maximum bonding energy which, in desorption, will lead to the highest hysteresis levels. As water molecules continue to penetrate into the material, they are superimposed in layers of water above the first, the bonding energy of which will be lower, leading to lower hysteresis. The evolution of hysteresis with humidity depends on the type of material, the fatliquoring agent applied and the effect of finishing. Results obtained are shown in Figure 3. It is observed that in crust leather, the non-fatliquored sample has the highest hysteresis, whereas for the finished leather, the sample fatliquored with the non-waterproofing fatty polymer showed the highest hysteresis.

Table IV shows the results of the absorption specific surface S (m^2/g) determined from the size of the estimated monolayer in absorption. It also shows the ratio between the size of the monolayer in desorption and absorption X_{md}/X_m , the mean value of hysteresis H (%) for water activities between 0.05 and 0.75 (mean of the curves of Figure 3). Also, the values of apparent density $Dens$ (g/cm^3) and tearing energy TE (m/mm^2 or N/mm) of the same samples^{5, 6} as structural parameters, which are characteristics of the leather are included.

Discussion

The influence of both fatliquoring and finishing operations on moisture absorption/desorption have been analyzed through variations induced on the GAB fitted models that can be attributed to these operations.

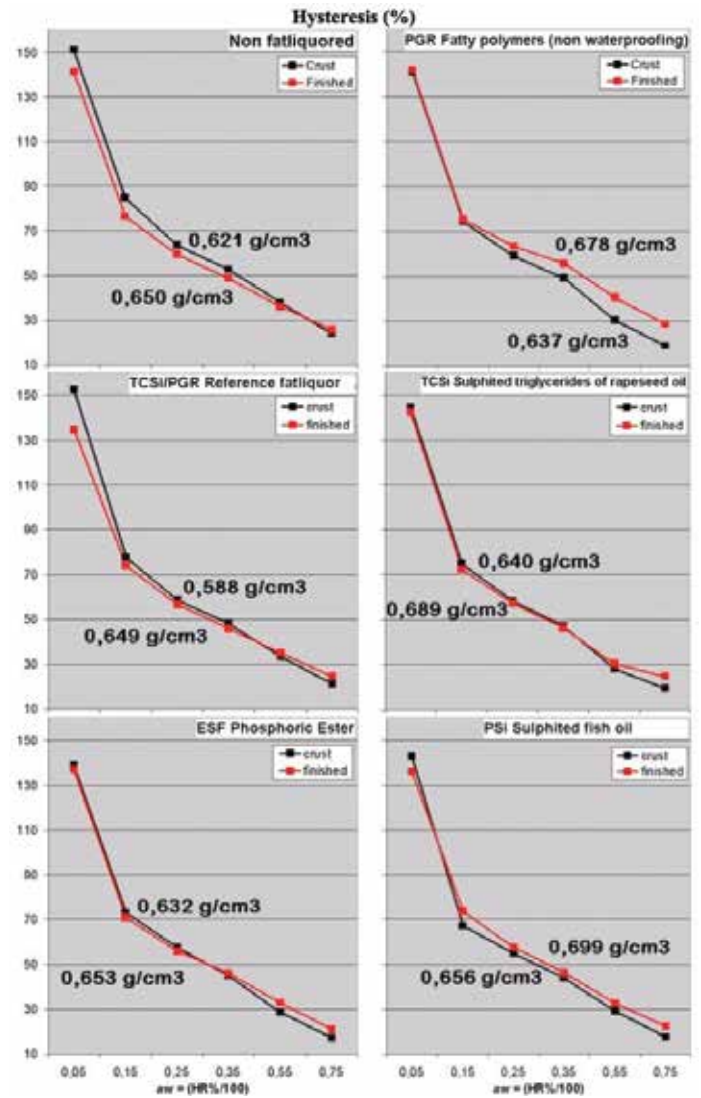


Figure 3. Hysteresis (%) according to water activity, fatliquoring agent and treatment step before (crust) and after finishing. The apparent density of leather is included.

Table IV

Specific surface of absorption S derived from the monolayer size measured in absorption X_m . Ratio between the monolayer sizes in desorption and absorption X_{md}/X_m . Mean value of hysteresis H for water activities between 0.05 and 0.75, apparent density $Dens$ of leather and tearing energy TE of non-fatliquored and fatliquored samples (see references in Table 2) before (in “crust”) C and after finishing F.

Parameters	Non fatliq'd		TCSi/PGR		TCSi		PGR		ESF		PSi	
	C	F	C	F	C	F	C	F	C	F	C	F
$S(m^2/g)$	374,2	335,5	401,5	319,2	350,1	291,9	375,6	282,0	370,6	311,8	354,0	313,9
X_{md}/X_m	0,96	1,37	1,16	1,35	1,23	1,34	1,24	1,44	1,19	1,29	1,22	1,31
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
$Dens(g/cm^3)$	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

Monolayer Size

There is no significant influence between the different fatliquoring agents on both absorption and desorption, although finishing significantly influences the reduction of the size of the monolayer. By observing Figure 4a, it can be seen that the size of the monolayer estimated in desorption is higher than the estimated in absorption. It is also seen, that the fatliquored samples before finishing show a monolayer size that is higher than after finishing and that the higher reductions correspond to the leather fatliquored with the non-waterproofing fatty polymer *PGR* and with the reference mixture *TCSi/PGR*.

The non-fatliquored sample shows a peculiar behavior. When this sample is subjected to a finishing operation, the monolayer size in absorption slightly decreases (as with the fatliquored samples) but the monolayer in desorption considerably increases. This could be explained by the protective effect of the fatliquors on the internal structure of the leather, the absence of which allows the formation of bonds between the different collagen micro fibrils thanks to the presence of water molecules that are attached to the various collagen chains, resulting in a higher rigidity of the leather structure.

Binding Energy Constant of the Monolayer

Also in this case, the energy constants in desorption are higher than in absorption. There is no significant influence of the different fatliquoring agents on this constant although the finishing operation significantly influences the reduction of the binding energy determined in both absorption and desorption. As observed in Figure 4b, the sample fatliquored with the non-waterproofing fatty polymer *PGR* suffers the highest diminution in the energy constants with finishing. This operation affects in the same way on both the non fatliquored and fatliquored samples. It should be pointed out the different evolution of the sulphited fish oil *PSi* with finishing. The binding energy in absorption slightly decreases with finishing while slightly increases in desorption contrary to what happens with the other samples.

Binding Energy Constant of the Multilayer

The different fatliquoring agents do not exert significant influence on the binding energy constant of the multilayer for both absorption and desorption (see Figure 4c). Contrary to what happened to the other parameters, the constants in absorption are higher than those in desorption. The finishing operation always increases this constant and, particularly, when leather has been fatliquored with the non-waterproofing fatty polymer *PGR*.

Average Hysteresis and Maximum Absorption Capacity at Saturation

Fatliquoring agents and the finishing operation do not exert significant influences on the evolution of the average hysteresis between absorption and desorption. On the contrary, both factors have a very significant influence on the maximum absorption capacity at saturation (Figure 4d). However, it can be observed that

the finishing operation: i) significantly increases the hysteresis of the leather fatliquored with the non-waterproofing fatty polymer *PGR*, ii) increases the hysteresis of the leather fatliquored with the sulphited fish oil *PSi*, iii) does not modify the hysteresis of leather fatliquored with phosphoric ester, *ESF* or with sulphited triglycerides of rapeseed oil, *TCSi* and iv) slightly decreases the hysteresis of the non fatliquored leather or that of the leather fatliquored with the reference mixture *TCSi/PGR* (cfr. Figure 3). Concerning the maximum absorption capacity at saturation, the highest values correspond to the non fatliquored sample followed by the group of samples fatliquored with the reference mixture *TCSi/PGR* or one of its components, the non-waterproofing fatty polymer *PGR*. Afterwards, the group of samples fatliquored with the sulphited fish oil *PSi* or with the phosphoric ester *ESF* have values of the maximum absorption capacity at saturation a little bit lower and finally the group of samples fatliquored with sulphited triglycerides of rapeseed oil *TCSi* that have the lowest values. In general, the finishing operation slightly decreases the maximum absorption capacity at saturation.

Size of the Absorption Monolayer and Apparent Density

The relationship between the apparent density of the leather and the size of the monolayer estimated by absorption is very significant (Figure 5a), so that the higher the density, the lower the internal surface of absorption, probably because of the greater difficulty of access of water molecules to the innermost surface of the leather. The finishing operation increases the apparent density of leather

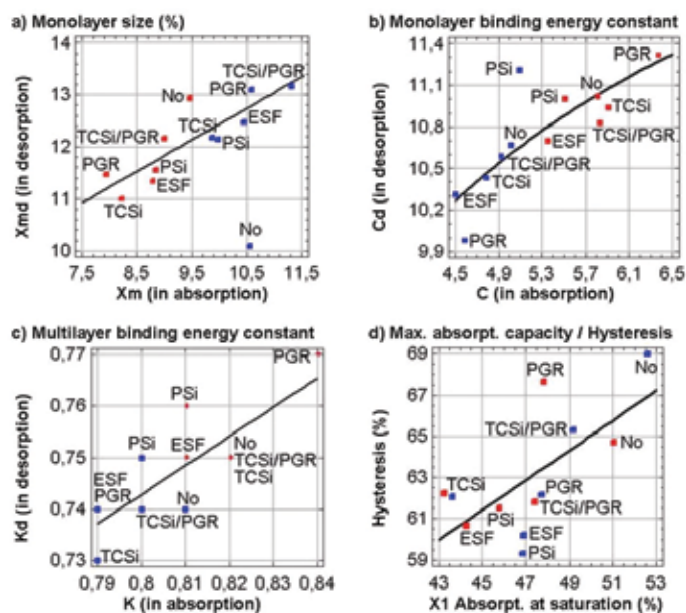


Figure 4. Relationships between absorption and desorption of the a) monolayer size, b) monolayer binding energy constant, c) multilayer binding energy constant and d) relationship between maximum absorption capacity at saturation and hysteresis, according to the fatliquoring agent (see references in Figure 3) before (blue dots) and after (red dots) finishing.

and diminishes the monolayer size, although this phenomenon is more remarkable in fatliquored leathers. This can be caused by the greater easiness of relative movement of collagen micro fibrils and the steric hindrances that can be exerted by the fatliquors that difficult linkages between water molecules and collagen. Among the finished leathers, the sample fatliquored with the *PGR* has the highest apparent density whereas the sample fatliquored with the *PSi* shows the lowest absorption monolayer.

Ratio Between Monolayer Size Estimations in Desorption and Absorption, and the Mean Hysteresis

The phenomena of water diffusion inside the leather are dynamic and the accessibility of water molecules to the bonding points to the collagen macromolecule implies the overcoming of steric hindrances that grows with the inclusion of fatliquoring agents and the higher density induced by finishing. The steric hindrances make difficult the diffusion of water towards the inner part and to outside of leather. The greater the diffusion difficulty, the higher the difference in the estimation of the monolayer in desorption and absorption and, therefore, a higher hysteresis should be expected.

Ratios between monolayer sizes up to the unity could be considered indicators of maximum easiness of diffusion due to the absence of steric impediments. Values higher than the unity would indicate the presence of steric impediments that hinder the diffusion of water molecules inside the material. In Figure 5b, two different behaviors in relation to the evolution of the ratio between monolayer sizes and mean hysteresis are observed: For crust leathers, the non fatliquored sample has the maximum accessibility but, also, the highest hysteresis. This is explained by the easiness with which water molecules can bind to the hydrophilic groups of collagen so that high hysteresis will respond not to steric hindrances but to the maximum binding energy. The values of the monolayer ratio in the crust fatliquored samples indicate that the estimates of the monolayer in desorption exceed 15 to 25% those of the estimates in absorption, with lower mean hysteresis values (60 – 65%). Here, the

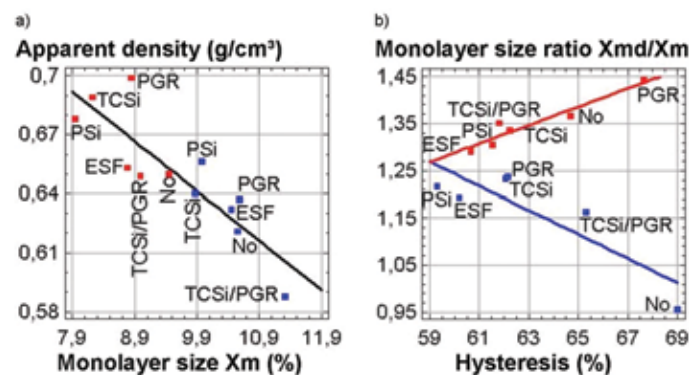


Figure 5. a) Relationship between size of the monolayer in absorption and apparent density, and b) mean hysteresis between 5% and 75% of relative humidity and ratio of the monolayer sizes in desorption vs. absorption, according to the fatliquor agent (see references in Figure 3) before (blue dots) and after (red dots) finishing.

presence of the fatliquoring agents hinder the binding of the water molecules to the collagen hydrophilic groups resulting in a diminution of the monolayer size and, particularly, the energy with which water binds to collagen, reducing hysteresis. The leather fatliquored with the reference mixture *TCSi/PGR* has a somewhat better level of accessibility than that of other crust fatliquored leathers, but with higher hysteresis, offering a better anchoring of the water in the leather. For crust leathers, Figure 3 shows that the non fatliquored sample has the highest hysteresis regardless of the level of environmental relative humidity (the absence of fatliquoring agents favors the fixation of water in the reactive groups of the leather) whereas for the sulphited fish oil *PSi*, the lowest levels of hysteresis are, in general, observed. For finished leathers, a close linear relationship between accessibility and hysteresis is observed so that the hysteresis increases with the X_{md}/X_m ratio i.e., with the greater difficulty of movement of the water molecules inside the leather. The highest hysteresis corresponds to the leather fatliquored with the non-waterproofing fatty polymer *PGR* and to the non fatliquored leather. For finished leathers, Figure 3 shows that the sample fatliquored with the non-waterproofing fatty polymer *PGR* has the highest hysteresis for different levels of humidity while the lowest values are given in leathers fatliquored with *TCSi* and *PSi* in situations similar to those of crust leathers. Here two effects are combined: first, the easiness of the fatliquoring agent for the internal rearrangement of the leather during the finishing operation by facilitating the migration of the collagen fibers between them, with the consequent reduction of free space for the diffusion of the water molecules towards the interior and, second, the decrease of the binding energy of water with the collagen that, in some cases, it can be enhanced by the finishing operation as in the *PGR* polymer.

Relationship Between Moisture Absorption/Desorption Characteristics and Tearing Energy

The tearing energy is a parameter that is characteristic of the internal structure of the leather⁽⁶⁾. It responds to the binding energy between the collagen fibers and the mobility between them. This parameter related to the compactness of the leather could have a behavior similar to that presented in relation to the absorption and desorption of moisture. From the regression analysis, it is observed that there is a significant linear relationship with the absorption at saturation X_I ($r = -0.74$). The higher the water absorption capacity, the greater the empty spaces in the interior and, consequently, the lower the tearing energy. From this relationship, other significant correlations can be observed: one with the apparent density ($r = 0.66$) and other with the monolayer size ($r = -0.62$). A more compact and tightened structure of the leather leads to better mechanical properties and hinders the exchange of moisture with the external environment.

Conclusions

After examining the influence of different fatliquoring agents and the finishing operation on the characteristic parameters of moisture absorption and desorption isotherms of leather and their possible

relationship with structural parameters such as apparent density and tearing energy, the following conclusions can be drawn:

- Finishing significantly affects the moisture absorption and desorption parameters, in particular those related water molecules that are directly linked to the reactive groups of the collagen forming the monolayer. Finishing reduces the size of the monolayer and increases the bonding energies of both the monolayer and multilayer.
- The sample fatliquored with the non-waterproofing fatty polymer *PGR* shows the highest descend in the energy constants with finishing. The sample fatliquored with sulphited fish oil *PSi* slightly decreases the binding energy in absorption after finishing, while increases slightly in desorption contrary to what happens with the other samples.
- The energy constant of the multilayer increases with finishing and, particularly, when the sample has been fatliquored with the non-waterproofing fatty polymer *PGR*.
- The maximum absorption capacity at saturation diminishes as a function of the fatliquoring agent and this capacity is also decreased by finishing.
- It is observed that the denser a leather, the lower the internal surface of absorption, probably due to the greater difficulty of access of the water molecules to its inner surface.
- The difficulty of penetration of water molecules inside leather and its fixation to the monolayer may be directly related to hysteresis. The stronger the linkage, the greater the difference in the estimation of monolayer size between desorption and absorption and, also, the greater the hysteresis.
- For finished leathers, a close linear relationship between accessibility and hysteresis is observed so that the hysteresis increases with the ratio of estimations of the monolayer between desorption and absorption, i.e., with the greater difficulty of migration of water molecules inside leather.
- The tearing energy is a characteristic parameter of the internal structure of leather and is significantly related to the absorption at saturation, apparent density and monolayer size. A more compact and tightened structure of leather favors the mechanical properties and hinders the exchange of moisture with the environment.

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