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Effect of Leather Finishing on Water Vapour Transmission. Part I. Water Vapour Transfer through Pigment Finished Leather

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In this paper the influence of soft leather coating thickness on moisture transmission behaviour is presented. It is shown that water vapour permeability decreases and sorption increases according to exponential law as coating thickness increases. The increase of water vapour sorption can be attributed to the decrease of top layer porosity, interaction of water molecules with leather collagen and acrylic polymer. The higher water amount in the leather permits the lower water vapour permeability. As water molecules amount becomes higher than that can bind to polymers, the clustering of water occurs. In the leather some cluster formation is observed only at high water vapour activity. In acrylic coating tendency to clustering is distinct. It is found that cluster size depends on the polymer nature and relative humidity.

Water vapour sorption behaviour may be classified as non-Fickian – "two-stage" sorption and it is characteristic for various coating thickness of leather. Changes in the leather surface topography in humid conditions depend on the coating thickness also: water accumulation increases thin-coated surface unevenness, while in the case of thick-coated surface unevenness decreases due to the expansion of the overall volume of coating and smoothing of embossed grain.

Keywords: leather, pigment finishing, coating thickness, water vapour permeability, water vapour sorption.

1. INTRODUCTION

Physical and mechanical properties of leather can be varied depending on the applications (footwear, gloves, clothing, purses, furniture upholstery, saddles, etc.). It is required that leather to be very soft, thin and extensible for gloves and clothing, more rigid for footwear, hard and stiff for soles, etc.

After to be dyed leather is subjected to finishing to improve wear properties of leather in general and to protect it from wetting and soiling, to level out patches and grain faults, to apply an artificial grain layer to splits or corrected grain leathers, to modify the surface properties (shade, lustre, handle, etc.) [1, 2]. For this purpose various finishing materials (casein, nitrocellulose, polyurethane, acrylic, other resin and polymer compositions) and techniques (glaze, plate, embossed, spray and curtain coating finish) can be used [2, 3].

In the case of pigment coating tanned leather is first coloured with a penetrating dye. The dye penetrates the surface of the leather giving it colour but not covering over natural markings. Then leather can be finished in one or more coating operations, with clear or pigmented finishes that do not penetrate the surface [3]. Pigment coat imparts the desired appearance of the leather and levels out the surface. Generally, the more finish leather has, the stiffer it becomes. Usually coating thickness does not exceed 0.15 mm.

It is been recognized that the moisture transport under a humidity transient is a key property influencing the dynamic comfort of the apparel: boots, clothes, and gloves. In the footwear water vapour transfer through leather, that is, perspiration, directly affects the thermal comfort of the foot [4, 5]. In great deal water vapour transfer is a result of the special properties of leather surface coating. The polymer coating must act as a barrier to liquid water entry from the environmental, but to be sufficient permeable to water vapour to allow significant amount of sweat to evaporate through leather.

The goal of this investigation is to study influence of leather finish coating characteristics on moisture transport properties in the exothermic conditions in order to predict comfortability of leather goods.

2. EXPERIMENTAL

Nappa leather – soft and thin leather, which can be applied for manufacturing of footwear, gloves and clothes – was used for the investigation of water vapour transmission. This leather surface was coated with opaque pigmented acrylic emulsion by spraying with compressed air [6].

To determine water vapour transfer versus coating thickness the pigment coat layers number was varied. In this way several types of coated leather were obtained. Their characteristics are presented in Table 1.

Nappa 0 is aniline leather – full grain leather that has been soaked in aniline dye, but does not have any subsequent pigmented finish coats applied. This dye penetrates the hide with colour allowing the natural grain to show through (Fig. 1, a). Aniline leather is the most natural looking leather with unique surface characteristics. *Nappa* 1 is semi-aniline leather, also attributed to the full grain leather, but more durable than aniline whilst still retaining a natural appearance and character imperfections (Fig. 1, b). The increased durability is provided by the application of the light surface coating, which contains a small amount of pigment.

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Table 1. Specification of the *nappa* leather test samples

Leather samples	Finishing level	Finished leather properties:		Coating properties:	
		Thickness d, mm	Apparent density ρ, mg/mm^3	Number of layers n (pigmented + topcoat)	Thickness h, μm
nappa 0	Non-coated leather	1.5 ± 0.12	0.45	0+1	2.7
nappa 1	Lightly finished leather		0.59	1+1	22.3
nappa 2	Middle finished leather		0.64	3+1	62.5
nappa 3	Fully pigmented leather		0.65	6+1	122.3

Pigmented leather is obtained by a polymer surface coating that contains pigments. This surface imparts greater wear resistance, water resistance and protection against the staining. Depending on the hide quality and requirements, it may be obtained full grain pigmented leather (*nappa* 2) and corrected grain pigmented leather (*nappa* 3) with the solid top layer. Full grain pigmented leather is leather whose natural grain has not been removed before applying a surface coating containing pigment (Fig. 1, c). Fig. 1, d presents corrected grain pigmented leather, which is obtained by sanding off a thin layer of the grain surface before the pigment coating is applied. Because this process removes surface blemishes, a lower grade of hide can be used. Because it also removes the natural grain pattern, an artificial grain is embossed onto the surface coating, although full grain pigmented leather is often embossed too.

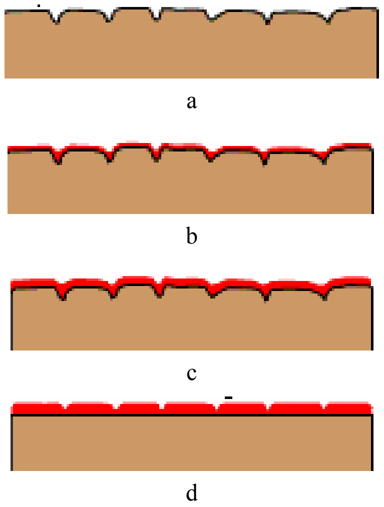

Fig. 1. Schematic representation of leather structure with various surface coating: a – non-coated leather; b – lightly finished leather; c – middle finished leather; d – fully pigmented leather

Finally, after pigment coating in all cases the topcoat with the acrylic lacquer layer was used. The topcoat determines the final appearance, the handle of the leather surface, and has decisive influence on the fastness properties of the finish.

Before the test all specimens were conditioned for at least 48 h at a standard atmosphere 20/65 (temperature $T = 20 \pm 2$ °C, humidity $RH = 65 \pm 5$ %) in accordance with LST EN 12222:1997. The water vapour permeability was measured according to EN 13515:2001 at constant temperature and relative humidity. A sample of leather was placed over a jar, which contained a solid desiccant – calcium chloride (Fig. 2). The whole set-up was placed upright in a conditioned chamber at 20 °C and relative humidity near to $RH = 100$ %.

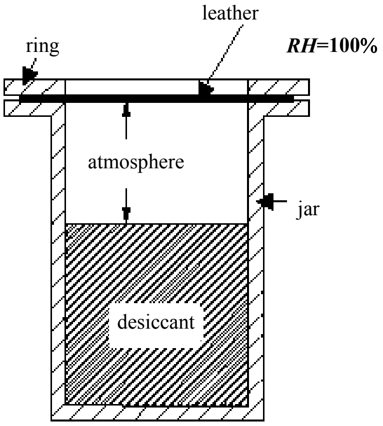

Fig. 2. Schematic representation of the cup for a test

An experiment takes typically not less than 16 h but not higher than 24 h. Then the jar is weighed in order to determine the mass of moisture that has passed through the test piece and been absorbed by the desiccant. Water vapour permeability P_{wv} was calculated from the equation:

$$P_{wv} = \frac{7639M}{d^2 t}, \tag{1}$$

where M is the increase in mass of the jar, d is the average diameter of the neck of the jar, t is the time between the first and second weighing.

For the determination of water vapour sorption according to EN 13515:2001 an impermeable material and the leather sample are clamped over opening of a container, which holds 50 ml water, for the duration of test. Water vapour sorption S_{wv} of the leather was determined by its difference in mass before and after the test:

$$S_{wv} = \frac{4\left(M_2 - M_1\right)\cdot 10^5}{\pi a}, \tag{2}$$

where M_1 is the initial mass of sample, M_2 is the final mass of sample, a is the internal diameter of the cylindrical container.

In order to determine the influence of leather coating on kinetics of water vapour sorption, test was continued up to 176 h until water droplets and humidity spots appeared on the leather surface. The changes in leather surface topography due to the water vapour sorption were examined by a standard image processing system, converting surface unevenness into soft lines.

3. RESULTS AND DISCUSSIONS

The internal climate, close to the skin, is hot and humid because the human body generates heat and moisture. The external climate is much drier and cooler. Consequently water vapour is driven from the inside to the outside.

Typically leather has an excellent moisture transport properties [7]. Finished leather surface is coated with polymeric material that forms the continuous phase and, therefore, is important for moisture transport properties, also. Besides, polymer coatings consist not only of polymer as a binder, but also pigments and other various additives, each of them affect moisture transport differently [8, 9].

The water permeability through leather depends on the coating thickness and, as a consequence, on the binder and pigment amount. The dynamic test of liquid water penetration, carried out according to EN 13518:2001, shows that in the case of light finished semi-aniline leather *nappa* 1 with small amount of pigment water penetration after 1 hour of testing exceeds even 118 %. While for *nappa* 2 it is lower than twice – only 51 %. Whereas full pigmented leather with high amount of pigment *nappa* 3 does not pass water even after 3 hours of testing.

No theoretical difference exists between sorption of liquid water and water vapour in the case of films and coatings if they are considered non-porous [10]. In porous media diffusion mechanisms are different for water vapour and liquid water [11].

As it is evident from Fig. 3, water vapour transfer and sorption properties of leather depend on the surface coating thickness. The increase of layer thickness favoured on the reduction of the leather permeability. In the case of lightly finished *nappa* 1 water vapour permeability P_{wv} is near to 41 g/m^2·h, while for fully pigmented *nappa* 3 it decreases almost twice – down to 23.7 g/m^2·h. On the other hand, only negligible difference between the water vapour permeability of the *nappa* 0 without pigment coating and lightly finished *nappa* 1 is observed (42 g/m^2·h and 41.1 g/m^2·h, respectively).

In the case of ideal pigmentation, when pigments are considered as non-hydrophilic, well dispersed, uniformly distributed through the coating film, and strongly bound to the binder polymer, the interface allows only minimal penetration. In such ideal system, water can only permeate by circumnavigation of the pigment particles, increasing the effective path length for diffusion and therefore lowering the permeability [12]. However, many pigmented coatings do not show ideal behaviour. Non-ideal behaviour includes hydrophilic and not fully dispersed pigments, including irregular distribution through the film and particle flocculation [12, 13]. Due to the hydrophilicity of pigment particles, pigments bound insufficiently to the binder, resulting in “vulnerable” interfaces. Water accumulation, i.e. water layer formation, around pigments causes expansion of the overall volume of the pigment and absorbed water. Within these interface liquid transport takes place, which is faster than diffusion through the binder matrix [12]. Consequently the water vapour permeability through pigment finished leather shows non-linear character. Besides, the non-linearity reflects interaction between water molecules and polymer chains (collagen and acrylates) as well. It was determined that the relationship between the water vapour permeability P_{wv} and the coating thickness of *nappa* leather can be approximated by the simple exponential equation ($R = 0.987$):

$$P_{wv} = 118.72\, e^{(-0.0013\, h)} - 77.82\,. \qquad (3)$$

So, the pigmented coating significantly lowers moisture transport. However, factors like incomplete dispersion, flocculation, and poor binding between pigment and polymer may diminish this effect [13].

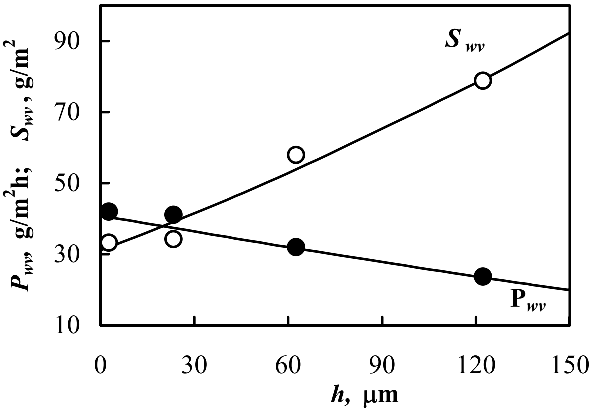

Fig. 3. Dependence of *nappa* leather water vapour permeability (P_{wv}) and sorption (S_{wv}) on the coating thickness h, μm: ●, ○ – experimental points; —— – theoretical curves

According to localized sorption theories, the penetrant is considered to bind at a specific sites in the polymeric structure, e.g. in cracks, pores, or at specific polar groups, which are capable to interact with polar penetrants like water [13].

However, the increase of pigment and polymer binder amount results on the deviation from the localized sorption behaviour. As can be seen from Fig. 3, at high humidity ($RH = 100$ %) the increase of leather coating thickness from 2.7 μm to 122.3 μm increases the water vapour sorption from 33 g/m^2 (*nappa* 0) up to 79 g/m^2 (*nappa* 3). In this case the sorption properties of *nappa* 0 and *nappa* 1 differ negligibly as well. It may be proposed that at the low coating thickness dynamic equilibrium, in which condensation of molecules onto bare site equals to the evaporation from occupied site, exists. The change of water vapour sorption S_{wv} on the *nappa* leather coating of thickness h can be described according to the below presented dependence with high correlation with the experimental results ($R = 0.984$):

$$S_{wv} = 134.65\, e^{0.0025 h} - 103.58\,. \qquad (4)$$

The increase of water vapour sorption can be attributed to the decrease of the *nappa* leather top layer porosity as the coating thickness increases. Besides, it depends on the interaction between water molecules and the hydrophilic leather collagen or acrylates in the coating layer.

Water molecules are highly dipolar. This character is due to the high electronegativity of oxygen compared to hydrogen. Partial electrostatic charges due to this difference in electronegativity result in strong interaction of water and other charged or polar groups and between water molecules mutually in leather. Both the types of interaction as well as the degree of interaction depend strongly on the polymer structure (leather and coating). It is generally accepted that for sorbed water molecules at least three different states are possible [13]: (1) single water molecules, which neither show significant interactions with other water molecules nor with their environment; (2) aggregated water molecules, which interact with each other to form agglomerates or clusters; (3) localized interaction of water molecules and polymer groups. Water transport in the hydrophobic materials usually proceeds according to states (1) and (2). For the hydrophilic polymers, such as leather and acrylic polymers, state (3) of absorbed water is characteristic. It is suggested that for highly hydrophilic polymers (3) is even subdivided into two states [14]: (3a) non-freezing water, i.e. water that is strongly bound to polar groups in the polymer and (3b) freezable bound water, i.e. water that is weakly bound to the polymer or to the non-freezing water. It may be suggested that for porous polymers, similar to other porous materials bulk water is present also.

On the other hand, for hydrophilic polymers clustering may be expected also, if the amount of water molecules in the polymer is higher than the quantity that can be bound to the polymer. For the qualitative interpretation of clustering Zimm-Lundberg cluster integral can be used [13]:

$$\frac{G_{ww}}{V_w} = -(1-\varphi_w)\left[\frac{\partial(a_w/\varphi_w)}{\partial a_w}\right]_{PT} - 1, \tag{5}$$

where G_{ww} is so-called cluster integral, V_w and a_w are the partial volume and activity of water molecules in the polymer, respectively, and φ_w is the volume fraction of water in the polymer.

The cluster integral indicates whether clustering takes place or not. For ideal solution, from Eq. (5) it follows that $G_{ww}/V_w < -1$, indicating that a particular water molecule does not affect the distribution of other water molecules. If $G_{ww}/V_w > -1$, there is a tendency to cluster. In this case, the concentration of water molecules in the neighbourhood of a given water molecule is higher than would be in the case for random distribution. Generally, the cluster integral is suited for weakly interacting penetrant-polymer systems.

In the case of hydrophilic polar polymers such as leather collagen, cluster integral is low $G_{ww}/V_w = -4.4$ [16]. So, water clustering does not take place for this material. However, at high water vapour activity ($RH > 95$ %) some water cluster formation may be observed. In acrylates tendency to clustering is distinct – depending on the acrylate structure and relative humidity the cluster integral varied in the range of $G_{ww}/V_w = 24 \div 287$ [16]. So, in the case of low coating thickness (*nappa* 0 and *nappa* 1) only negligible water clusters formation can be observed at high relative humidity. High amount of absorbed water is absorbed at the leather and coating interface due to the significantly lower permeability of polymer layer.

The Eq. (5) can only be applied for comparative purpose. For the quantitative evaluation of water clustering in the hydrophilic polymers the group of Favre and Perrin proposed a model [13, 15]. They characterize clustering in terms of a 'mean cluster size' (MCS) as a function of penetrant volume fraction φ:

$$MCS = \frac{(1-\varphi)(k_2\varphi+1)\ln(k_2\varphi+1)}{k_2\varphi} + \varphi. \tag{6}$$

In this relation, $k_2 = (k_s - k_p)/k_p$, where k_s is the penetrant-penetrant interaction parameter, k_p is the interaction parameter between polymer and penetrant, comparable to the Flory-Huggins interaction parameter χ [13].

Certainly, the cluster size depends on the polymer nature and humidity: for various structure acrylates $MCS = 1.09 - 1.27$ at $RH = 30$ % and $MCS = 1.22 - 1.50$ - at $RH = 50$ %. In the case of collagen MCS values are significantly lower: they vary from 0.62 at $RH = 20$ % up to 0.89 at $RH = 50$ % [16].

The overall solubility of water in the coated material is determined by the amount and nature of polar groups in the coating polymer and leather. Hydroxyl, carboxyl and peptide groups were found to bind water molecules strongly [13]. So, water molecules join to the carboxyl groups in acrylates and peptide groups, characteristic for leather.

From Fig. 4 it is evident that water vapour sorption increases as permeability decreases. It was determined that the simple correlation exists between the coated *nappa* leather water vapour permeability P_{wv} and sorption S_{wv}:

$$S_{wv} = 134.65(P_{wv} + 77.82)^{-1.92}\, e^{9.17} - 100. \tag{7}$$

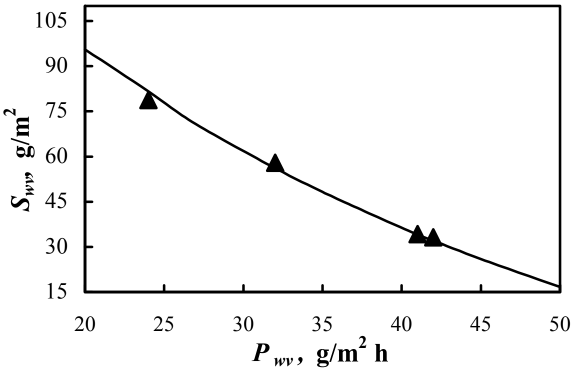

Fig. 4. Relationship between *nappa* leather water vapour permeability P_{wv} and sorption S_{wv}: ▲ – experimental points; —— – theoretical curve

The mathematical evaluation shows that the experimental data is in the high agreement with theoretical one ($R = 0.998$).

In order to characterize the water vapour sorption behaviour from the coating thickness the relative weight gain was plotted as a function of the square root of time for leathers *nappa* that were subjected to the penetrant activity a long time. The obtained results are presented in Fig. 5. Non-Fickian behaviour – "two-stage" sorption is characteristic for different finished *nappa* leathers. In this case the sorption is composed of two different parts: (1) fast Fickian sorption and (2) slow non-Fickian sorption [13, 17].

As can be seen from Fig. 5, the plots are Fickian until the moment they come to the level off – roughly after 40 h of the exposure at high humidity atmosphere ($RH = 100$ %). Evident that sorption rate in the fully pigmented leather is significantly higher than that in the light or middle finished leather. After 40 h of exposure the weight of *nappa* 1 reaches 57 g/m^2 and 69 g/m^2 for *nappa* 2, when in the case of *nappa* 3 – even 150 g/m^2.

It is obvious that for *nappa* 1 and *nappa* 2 leathers the water vapour sorption follows in the similar mode. So, the increase of coating thickness up to ~62 μm only negligible influences on the leather sorption behaviour.

After the reaching first saturation level the sorption curves are extended through non-Fickian part. The plot of *nappa* 3 starts to level off again after 112 h at $RH = 100$ %. However, in the case of the low coating thickness (*nappa* 1 and *nappa* 2) the weight continues to increase due to the high surface permeability and saturation is not reached yet after 176 hours of the exposure.

Berens and Hopfenberg proposed diffusion-relaxation model of two-stage sorption [13]. They considered the sorption process to be composed of two phenomenologically independent contributions: a diffusion part $M_F(t)$ that is governed by Fick's law and structural part $M_R(t)$, resulting from polymer relaxations. The total weight gain at the time t may be expressed as the linear superposition of these contributions:

$$M(t) = M_F(t) + M_R(t) \quad . \tag{8}$$

$M_F(t)$ can be given from the solution of the diffusion equation, known as the general Fick's law [4, 13, 17]:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D(C)\frac{\partial C}{\partial x} \right), \tag{9}$$

where C is the penetrant concentration, t is the time, x is the position in the film in the direction of diffusion, and D is the diffusion coefficient or diffusivity of the penetrant in polymer. D is the pivotal parameter determining the rate of transport.

It is assumed that more than one independent relaxation process is possible, so $M_R(t)$ is given by

$$M_R(t) = \sum_i M_{\infty,i}\left[1 - e^{-k_i t}\right], \tag{10}$$

where $M_{\infty,i}$ represents the equilibrium sorption due to the i-th relaxation process, and k_i is the first order relaxation constant of the i-th relaxation process. Originally, this model (Eq. (10)) has been developed for diffusion in spherical particles, but it has also been applied to diffusion in polymer films [17].

The changes in the leather surface topography upon exposure time at humid conditions depend on the coating thickness, also. The highest surface roughness is characteristic for the full grain leather *nappa* 1 with thin coating layer (Fig. 5, 1_b). The increase of coating thickness decreases leather surface unevenness and in the case of corrected grain pigmented leather *nappa* 3 only negligible irregularities are observed (Fig. 5, 3_b).

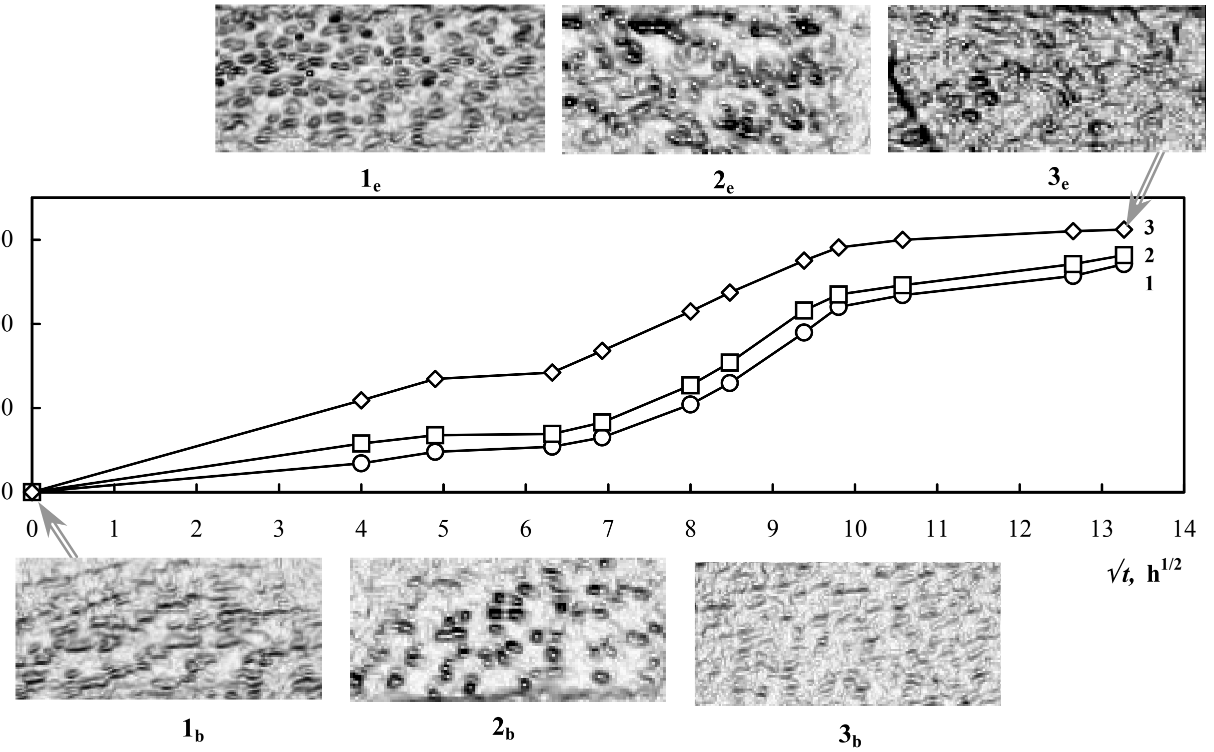

Fig. 5. Dependence of the pigment finished leather water vapour sorption and changes in surface topography upon the exposure time at $RH = 100$ %: 1 – lightly finished leather *nappa* 1; 2 – middle finished leather *nappa* 2; 3 – fully pigmented leather *nappa* 3 (1_b – 3_b – before sorption; 1_e – 3_e – at the end of sorption test) (Magnification ×20)

Accumulation of water molecules causes expansion of the coating layer of leather. The changes of the surface topography upon water action are more visible in the case of thin coating layer, also (Fig. 5, 1_e). It is due to the grain swelling that increases unevenness of the surface. Meanwhile in the case of *nappa* 3 permeability of coating layer is low, so accumulated water at the interface affects on the smoothing of embossed grain on the surface coating. Therefore, only negligible changes are observed in the surface topography of nappa 3 (Fig. 5, 3_e). It is necessary to mention that at the end of sorption test the surface of leather samples becomes deeper due to the condensed water.

The water vapour permeability depends on the water concentration in the leather. As can be seen from Fig. 6, the increase of the exposure time at $RH = 100$ % decreases water vapour transmission possibility.

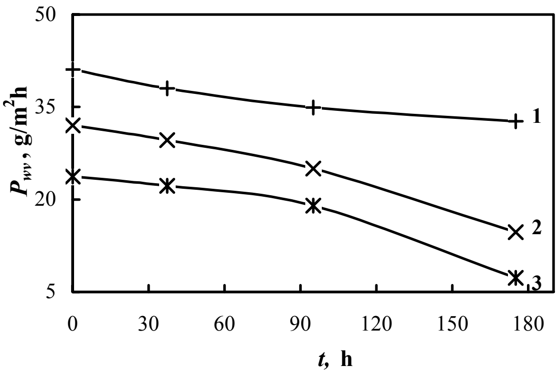

Fig. 6. Dependence of water vapour permeability upon exposure time at $RH = 100$ %: 1 – *nappa* 1; 2 – *nappa* 2; 3 – *nappa* 3

However, in the case of thin-coated leather the decrease of permeability proceeds in lower rate (21 % for *nappa* 1 as compared to 54 % and 70 % for *nappa* 2 and *nappa* 3, respectively). Thin coating layer creates good conditions for the evaporation of water vapour molecules from the occupied site. So, only insignificant decrease of water vapour permeability is characteristic in the case of thin-coated leather. Besides, the higher exposure time the higher decrease intensity of water vapour permeability.

CONCLUSIONS

Moisture transfer rate and character through leather depends on special properties of the surface coating.

Depending on the coating thickness water vapour permeability through the leather and sorption vary according to the exponential law. Pigment coating significantly lowers moisture transport in the leather.

The increase of water vapour sorption can be attributed to the decrease of coating layer porosity, interaction of water molecules with the leather collagen and acrylic polymer. The higher water amount in the leather inspires the lower water vapour permeability through leather.

Water clustering does not take place for leather. However, at high water vapour activity some water cluster formation is observed, because amount of water molecules is higher than that can be bound to the leather. In acrylic coating tendency to clustering is distinct. Cluster size depends on the polymer nature and relative humidity: in acrylic polymer cluster size is significantly higher compared to that in leather.

"Two-stage" sorption behaviour, which is composed of fast Fickian sorption and slow non-Fickian one, is characteristic for leather with various coating surface thickness. Water accumulation increases thin-coated surface unevenness, while unevenness of thick-coatings decreases due to the smoothing of embossed grain by the expansion of layer volume.

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