ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 10, No. 3. 2004

Effect of Leather Finishing Technology on Water Vapour Transmission. Part II. Water Vapour Transfer through Microporous Film Laminated Leather

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Received 25 September 2003; accepted 22 September 2004

The water vapour transfer through microporous film laminated leather has been investigated. Water vapour transmission is a multi-stage process, consisting of penetrant absorption, solubility, desorption and diffusion. Adhesively bonded microporous film does not worsen moisture transfer properties of the laminated leather. Notwithstanding water vapour permeability decreases and absorption increases due to the nonporous adhesive layer. In laminated leather and its layers water vapour absorption may be classified as non-Fickian: sigmoidal – for microporous film and two-stage – for all leather samples.

Water vapour accumulation at the leather/adhesive layer interface causes the adhesion loss of coating polyurethane film and changes in the failure mode. Water vapour induced film delamination begins at the weakened sites of the interface (i.e. small cavities, voids, and topographical irregularities of leather, etc.). Under driving gradient the local accumulation of interfacial water expands and multi-layers of water molecules build up. The splitting of the interfacial water layers begins the loss of adhesion. At long penetrant activity at both sides the film delamination propagation and blister formation in the laminated leather may occur.

Keywords: laminated leather, coating film, penetrant, water vapour permeability, absorption, adhesion loss.

1. INTRODUCTION

Permeability is a key property in polymer for many applications. In packaging, the polymer materials are generally required to have low permeability to gases and vapours. The barrier property is also crucial for polymer tubing used in fluid transport. Nevertheless, in some special applications, high permeation rates to certain species are required. In separation process by polymer membranes, high permeability ensures high productions of valuable chemicals per unit area of membranes surface. In other cases, high comfort of humans in situations where water vapour build-up and water condensation are to be avoided is obtained with breathable films, which allow water vapour to go through at a high rate [1 – 5]. These breathable films possess rather high water vapour permeability, while acting as a barrier towards liquid water. A wide range of breathable membranes is used [6 – 11]. Examples of applications for breathable films are: protective clothing such as jackets, gloves and boots, diapers and feminine hygiene, roofing membranes, photographs, etc.

Usually tanned leather is coated with thin pigmented or lacquer coatings [12]. One of the purpose of such coating is decorative, another – to protect it from wetting and soiling, to level out patches and grain faults.

The other rarely used method of leather coating is surface lamination with polymeric film. In this case, film is adhered to the leather surface by pressing with hot plate [13].

The investigation of water absorption and diffusion is necessary to predict material behaviour in damp conditions, for wearing properties estimation in the stage of materials selection [1, 2]. Large number of methods are available for the measurements of gases and water permeability through polymer films [3, 7, 8, 10, 14].

Water vapour transfer through a leather, and consequently footwear upper system, directly affects the thermal comfort of human foot [15,16]. As it was shown earlier, water vapour transfer in great deal is a result of the special properties of leather surface finish technique [17].

In a present paper the attempt to reveal the changes in water vapour transfer behaviour at various stages of laminated leather production was made.

2. EXPERIMENTAL

Laminated leather – *Permair* leather – used in this study was a commercial grade product. Laminated leather was obtained by hot pressing of microporous polyurethane (PU) membrane to ground-coated split leather surface. Film bonding was performed by water-born polyurethane adhesive. Polymeric film provides protection against stuffs, stains and water, influenced on the mechanical properties [18]. It comprises about 1/3 of laminate thickness. The structure of laminated leather and its comparison with pigment finished leather is presented in Fig. 1. As it can be seen laminated leather is similar to full top grain leather.

For investigations semi-finished products of laminated leather at various stages of its production were used. Some characteristics of all investigated materials are given in Table 1.

Before test all specimens were conditioned in standard atmosphere in accordance with the requirements of LST EN 12222. The water vapour permeability was measured according to ISO 14268 at a constant temperature and relative humidity. A sample of material was placed over a container, which contained a solid desiccant (Fig. 2, *a*). The whole set-up was kept upright in

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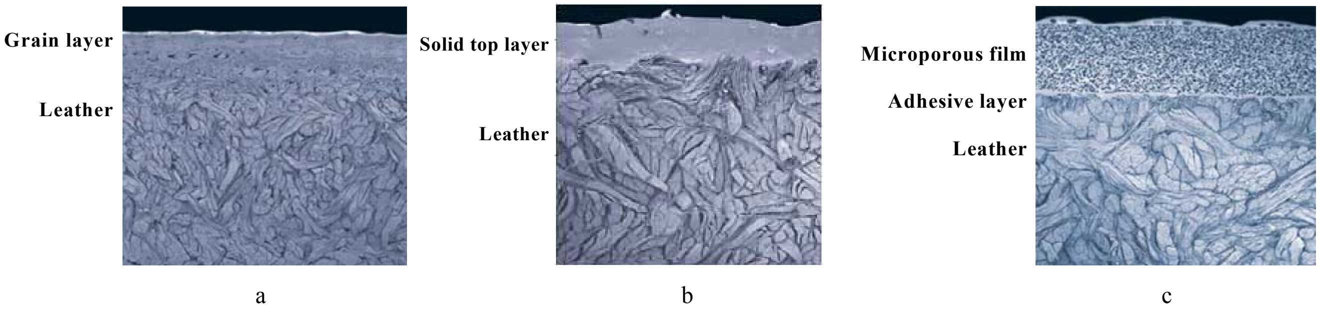


Fig. 1. Structure of leather different finishing: a – full top grain leather; b – corrected grain leather; c – microporous film laminated leather

Table 1. Characteristics of materials at the different stages of laminated leather production

Materials	Properties	
	Thickness, mm	Apparent density, mg/mm^3
Split leather	1.37	0.54
Ground-coated split leather	1.47	0.68
Ground-coated leather with adhesive layer	1.63	0.72
Microporous PU film	0.43	0.03
Laminated leather	1.69	0.50

a conditioned atmosphere at a temperature of 20°C ± 2 °C and relative humidity of 65 % ±5 %.

For the determination of water vapour absorption according to ISO 17229 an impermeable material (barrier) and the test piece is clamped over opening of a container, which holds water, for the duration of test (Fig. 2, *b*). Water vapour absorption behaviour of the leather was determined by changes in mass before and after the test.

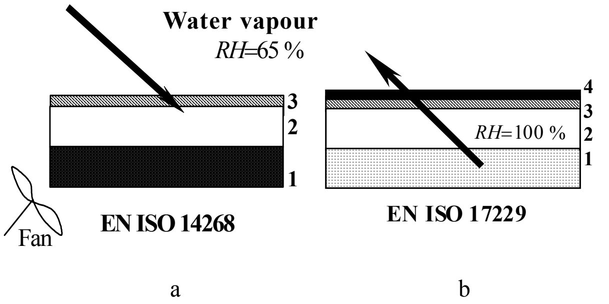


Fig. 2. Schematic representation of the test methods used in the present study (a: 1 – desiccant, 2 – atmosphere, 3 – specimen; b: 1 – water, 2 – atmosphere, 3 – specimen, 4 – barrier)

To determine the influence of coating film on the water vapour absorption behaviour test (Fig. 2, *b*) was continued until water droplets and humidity spots appeared on the tested material surface (up to 180 h). The test was prolonged up to 620 h to determine the influence of the water vapour absorption on PU film adhesion to split leather surface. In this case delamination test of PU film from split leather surface was carried out (according to LST EN 13514) after absorption.

3. RESULTS AND DISCUSSIONS

3.1. Water vapour permeation process

The internal climate, next to the skin, is warm and wet because the foot is generating heat and moisture during walking. The external climate is much drier and cooler. Consequently water vapour (perspiration) is driven from inside of the footwear to outside.

Polymeric material forms the continuous phase of a leather coating and, therefore, is important for transport properties. Besides, polymer coatings consist not only of polymer as a binder, but also of various additives, each of them affect on moisture transferring differently [9, 19].

Notwithstanding the coating film is perforated with tiny microscopic holes or pores [6, 8], laminated leather is highly resistant to the water penetration. Dynamic test of water penetration (in accordance with ISO 5403) shows that water does not penetrate through leather even after 4 – 6 h of dynamic testing. The pore size is sufficiently small (about 5 μm) and water does not pass through. However, small water vapour molecules can permeate through these pores [20].

Generally, water vapour transmission through the polymeric material is a multi-stage process. In the case of permeable polymer material, water vapour (penetrant) at first is absorbed into material surface, then solubilized into the polymer matrix and, finally, diffused through the matrix under a concentration gradient. It may be noticed that *solubility* refers to the amount of penetrant being taken up into solid material structure (not dissolved).

The data of the water vapour permeability P_{wv} investigation at different stages of laminated leather production are shown in Table 2. It is evident that split leather shows highest water vapour permeability properties. The ground coating of split leather practically does not worsen the permeability, while adhesive layer reduces the P_{wv} almost four-fold. The water vapour permeability through PU film is significantly lower than that through uncoated leather (18 g/m^2·h compared to 40 – 42 g/m^2·h). However, P_{wv} of microporous film shows significantly higher water vapour permeability than other polymeric films used for coatings (e.g. 0.3 – 0.5 g/m^2·h) [1].

On the other hand, the PU coating film has higher water vapour permeability compared to that of split leather coated with adhesive layer. Similar value of P_{wv} is characteristic for PU film laminated leather. So, it may be supposed that adhesive forms nonporous barrier, which significantly reduces water vapour permeability through the laminated leather.

As can be seen from data presented in Table 2, water vapour absorption S_{wv} of PU microporous film is low – only 2 g/m^2. Absorption of split and ground coated leathers is significantly higher due to the high interaction of leather with water molecules. However, the coating of split leather surface with adhesive layer increases water vapour absorption almost twice comparing to that of uncoated leather. As in the case of water vapour permeability, the water vapour absorption of laminated leather is comparable with that of split leather with adhesive layer. It allows to confirm the assumption that the absorption increases due to the water vapour condensation and accumulation near low permeability adhesive layer.

Table 2. Water vapour permeability and absorption of laminated leather components

Component	Permeability P_{wv}, g/m^2·h	Absorption S_{wv}, g/m^2
Split leather	42.0	34.2
Ground-coated split leather	40.0	39.5
Ground-coated leather with adhesive layer	10.3	67.0
Microporous PU film	17.7	2.0
Laminated leather	10.2	63.9

So, coating PU film does not worsen moisture transport properties of laminated leather, while adhesive layer, used for this film bonding to leather surface, acts as nonporous barrier and decreases water vapour permeability increasing its absorption capacity.

Multi-stage permeation process in the microporous PU film laminated leather due to nonporous adhesive layer proceeds according to another mechanism than presented above. In later case water vapour (penetrant) is:

- absorbed into leather surface,
- solubilized into leather structure,
- diffused through the leather under a concentration gradient,
- desorbed from the leather into the interfacial region between the leather and adhesive film,
- solubilized into the polyurethane adhesive layer,
- partly diffused through the adhesive layer and porous PU film.

It is clear that the rate of permeation depends on two independent parameters of laminated leather: the solubility of the penetrant in leather and its ability to pass through the laminated leather layers.

The solubility of water in polymer is governed by the same thermodynamic law that dictate the solubility in thermoplastic polymers in solvents or miscibility of two different solvents. That is, the process depends on the relative strength of the attractive forces between any two molecules of water and any two molecules of polymer. The presence hydroxyl and peptide groups in the leather facilitate absorption of water vapour. On the other hand, water vapour permeation rate in adhesive and coating films increases due to carboxylic, ester groups, and to less extent, the amide groups of urethane. Besides, water solubility will occur only in the amorphous segments of polyurethane [21].

Depending on material structure water vapour diffusion may be described as activated (homogeneous) and non-activated (heterogeneous) [21, 22]. In the leather and PU film non-activated diffusion through materials pores and capillaries is the primary mechanism by which water vapour is transfered.

Water vapour activated diffusion depends on the thermodynamic interaction between water and material to be penetrated, the affinity one for the other. Activated diffusion rate is also effected by polymer polarity, crystallinity, chain stiffness, cross-link density, etc. [21]. In nonporous polyurethane adhesive film water vapour transport mainly occurs through activated diffusion. On the other hand, activated diffusion proceeds in the porous layers of laminated leather, also.

3.2. Water vapour absorption mechanism

Different permeation of the laminated leather layers possesses different absorption kinetics during exposure to high humidity.

Generally, in kinetic absorption experiments a quantity representing overall penetrant loss or gain for investigated materials is recorded as a function of the square root of time. The water gain kinetics for laminated leather and its separate layers (split leather and polymeric coating film) as a function of the square root of time is presented in Fig. 3. In all investigated cases water vapour absorption may be classified as non-Fickian according to the appearance of presented kinetics plots.

The free porous PU film is subjected to the penetrant activity at both sides. The transfer process in the film is Fickian, but due to slow establishment of equilibrium at the surface of the film, kinetics appears anomalous [23]. The saturation level in the film is reached after 160 hours of exposure at the humid conditions. As can be seen, the water vapour absorption kinetics is more similar to sigmoidal model – non-Fickian behaviour (Fig. 3, curve 1). The absorption curve is S-shaped, showing the point of inflection roughly after 40 h of testing.

The surface topography of investigated materials before and after water vapour absorption test was examined by standard image processing system. Water droplets are seen on both sides of PU film surface – water vapour molecules transfer through polymeric film pores. Attraction between water molecules forces molecules to group together in a droplet.

Another mode of non-Fickian behaviour – "two-stage" absorption is characteristic for all samples of leathers – split and laminated. In this case the absorption is composed of two parts: fast Fickian absorption S_F and slow non-Fickian absorption S_R [17, 23]. As it can be seen, the curves are Fickian from the start until the moment it starts to level off – roughly 48 h. After reaching saturation level the absorption curves are extended through non-Fickian part. Ultimately, saturation in all samples of leathers is reached approximately at the same time as in the film, i.e. after 160 h.

Depending on the leather finishing level difference in the absorption kinetics can be observed. The plot of ground-coated leather (without coating film) is below the plot of laminated leather (Fig. 3, curve *2*). It occurs due to markedly high water vapour permeability of non-coated leather. Besides, in this case the second stage starts after plot levelling off after 48 h and proceeds slower up to 72 h of exposure at humid conditions. Then water absorption rate increases until the reaching saturation level.

In this case of laminated leather (Fig. 3, curve 3) water gain is higher due to the influence of nonporous adhesive layer, which, as it was shown above, acts as a barrier towards water and causes its condensation and accumulation in the leather. It can be seen from the changes in laminated leather surface topography. Before absorption laminated leather surface roughness is caused by the split leather surface texture and the imperfections of film bonding process. After exposure to $RH = 100$ % the increase in leather surface roughness is evident. In this case water condensation and accumulation in small cavities, voids, and topographical irregularities, etc. cause expansion of leather structure and unevenness of surface increases.

It was determined that weight uptake by various leathers (non-coated and laminated) at the Fickian part may be expressed by equation:

$$S_F = k_{S1} \cdot \tau^{0.5} - k_{S2} \ , \tag{1}$$

where k_{s1} and k_{s2} are the absorption constants. The investigations showed that value of these constants increases as material absorption decreases.

To describe water vapour absorption kinetics of various leathers and PU film in the non-Fickian region below presented function was adopted:

$$S_R = (k_{R1} + k_{R2} \cdot e^{-\tau})^{-1} \, , \tag{2}$$

where k_{R1} and k_{R2} are the relaxation constants, which depend on material nature.

The differences in leather absorption curves may be caused by different moistened surface nature and, therefore, different water transmission character. Thus, the changes of the water vapour permeability of leather and polyurethane film in the process of water absorption was investigated (Table 3).

The obtained results show that in all cases permeability decreases when exposure duration to humid conditions increases. Lowest effect on the changes of water vapour permeability was observed in the case of microporous PU film. It decreased by 30 % after 175 h of exposure, while in the case of ground-coated leather and laminated leather – in 2.5 – 2.8 times.

Table 3. Changes of water vapour permeability of laminated leather and its layers during absorption process

Component	Permeability P_{wv}, g/m^2·h after exposure to $RH = 100$ %		
	40 h	95 h	175 h
Ground-coated split leather	40.0	28.0	14.3
Microporous PU film	13.7	10.2	9.5
Laminated leather	10.2	9.6	4.0

The lamination of leather effected not only the rate of water vapour absorption (i.e. film barrier properties), but leather mechanical properties, also [18]. As it was assumed earlier, the most critical location of water is the leather/adhesive film interface. It may be supposed that water accumulation at the interface will cause changes in system mechanical properties due to the film delamination from the leather surface.

In Fig. 4 the dependence of PU film peel strength upon laminated leather exposure duration to high humidity conditions ($RH = 100$ %) is presented. As it can be seen,

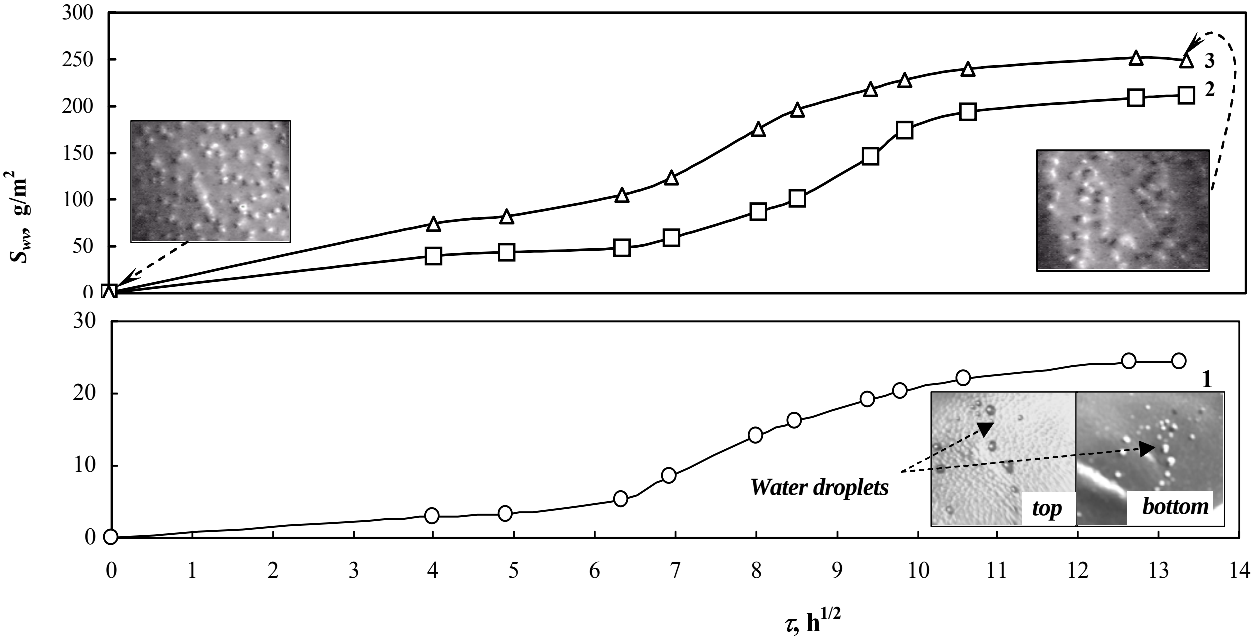


Fig. 3. The water vapour absorption kinetics for laminated leather and its components: 1 – microporous film; 2 – ground-coated leather; 3 – laminated leather

the exposure up to saturation level – approximately after 160 h – does not influence peel strength and failure mode (cohesion in the film).

However, further increase of exposure duration effects the adhesion decrease between PU film and split leather. After 625 h the adhesion decreases more than 10 %.

Besides, the failure mode of adhesive joints changes into mixed mode – into the cohesion in PU film and into the adhesion at the interface (50/50 by area). It can be supposed that condensed water at the leather/film interface weakens bonds between film and leather and, at the end, causes their failure [21].

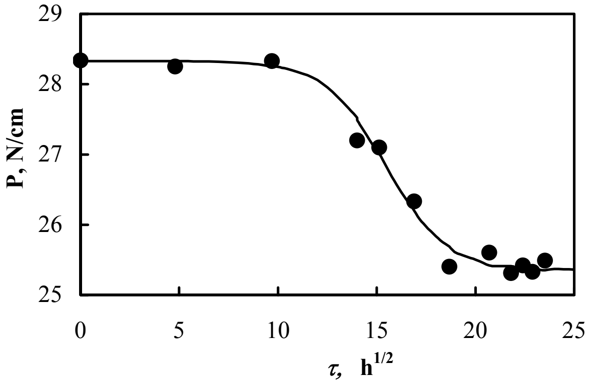
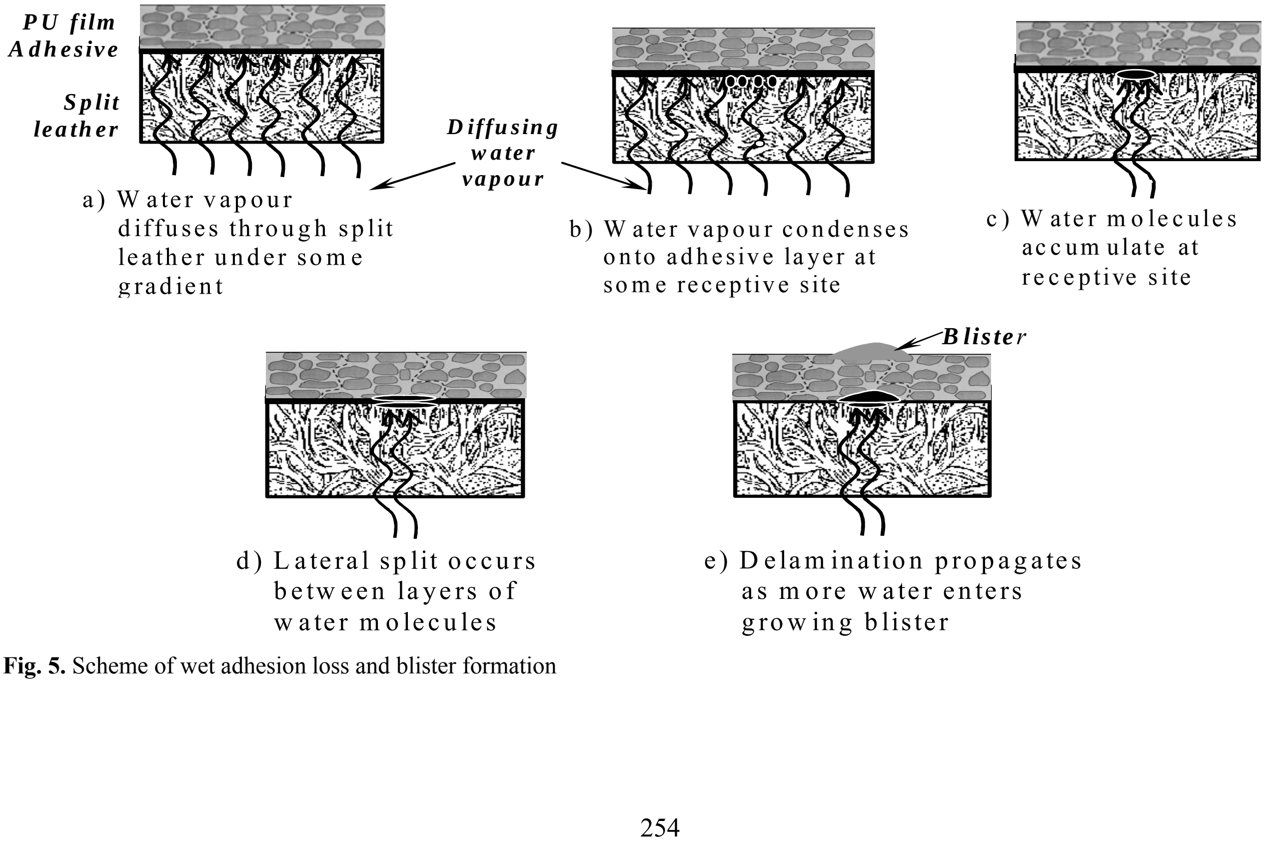


Fig. 4. Dependence of peel strength between split leather and PU film upon the absorption duration

The model of wet adhesion loss with blister formation in coated systems has been proposed by Leidheiser and Funke [22]. Their model requires 3 conditions: 1) through-way pathway for water transport, 2) subfilm site for initiation of water accumulation, and 3) driving force to facilitate the direct transport of water. According to this model adhesion loss initiates as water accesses the sub-line and propagates with water accumulation in multiple layers at the interface. Eventually, this multi-layered accumulation of water splits. Then, it undergoes a lateral peeling propagation into film areas surrounding the original site of delamination as further volumes of water accumulate and the leading edge of the forming blister is mechanically stressed. So, according to Leidheiser and Funke coating film adhesion loss model includes initiation, accumulation, splitting, and blistering propagation.

Similar model can be proposed to explain film adhesion loss in the laminated leather due to water vapour diffusion (Fig. 5, *a*). Water vapour induced film delamination in the laminated leather probably begins at weakened sites at the interface with adhesive layer, where water vapour passes through split leather and condenses at leather/adhesive interface due to low permeability of adhesive layer (Fig. 5, *b*). Such sites are most likely sub-microscopic, discrete. They may be small cavities, voids and fissures in the split leather structure, microscopic areas because of wetting difficulties by adhesive or topographical irregularities of leather surface. They may be sites where bonding has ruptured due to external stress effects such as impact or other deformation. Under such conditions water molecules in the laminated leather, which has absorbed water, may interpose themselves before reformation of the bond between film and leather. This leads to condensation and sites of water accumulation (Fig. 5, *c*).

The localized accumulation of interfacial water will increase under a variety of driving forces. These forces are primarily osmotic gradients, but also temperature gradients, etc. [24]. Under one or more of various driving gradients the local accumulation of interfacial water expands and multi-layers of water molecules build up (Fig. 5, *d*). Actual delamination occurs within the growing water layer, only after accumulation has increased to several molecular layers thickness. Such splitting of interfacial water layer starts the loss of adhesion.



a) Water vapour diffuses through split leather under some gradient

b) Water vapour condenses onto adhesive layer at some receptive site

c) Water molecules accumulate at receptive site

d) Lateral split occurs between layers of water molecules

e) Delamination propagates as more water enters growing blister

Fig. 5. Scheme of wet adhesion loss and blister formation

The continued transport of water vapour through the leather to the site of delamination results in further accumulation, so that peeling forces are increased at the interface of film and leather around the periphery of the immediate site of blister initiation. The initial localized delamination is propagated into surrounding areas, a process that is macroscopically identified as blister formation (Fig. 5, *e*).On the other hand, propagation of PU film delamination and blister formation in the laminated leather can be observed only in the case of very long penetrant activity at the both sides. Commonly, homogeneous and heterogeneous diffusion in porous and nonporous laminated leather layers result in high water vapour transmission rate without blister formation.

CONCLUSIONS

1. Microporous polyurethane film laminated leather shows peculiar multi-stage water vapour transmission behaviour.
2. Water vapour absorption in laminated leather and its separate layers can be classified as non-Fickian: sigmoidal – for microporous film and two-stage – for leather samples.
3. Microporous coating film does not worsen moisture transmission of laminated leather, while adhesive layer, used to bond film, decreases the water vapour permeability and increases its absorption due to the formation of nonporous barrier.
4. Water vapour condensation and accumulation at the leather/adhesive layer interface induces adhesion loss of coating film.
5. Polyurethane film delamination starts at weakened sites of the interface (small cavities, voids, leather topographical irregularities, etc).
6. The local accumulation of interfacial water expands under driving gradient and multi-layers of water molecules build up. The splitting of the interfacial water layers initiates the loss of adhesion.
7. At long penetrant activity from both sides the film delamination propagation may occur.

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