WATER VAPOR PERMEABILITY OF BOVINE LEATHER FOR MAKING PROFESSIONAL FOOTWEAR

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Abstract

Different methods were used to investigate water vapour resistance and water vapour permeability on several bovine leathers to be used for making professional footwear. The Permetest instrument determined water vapour resistance while water vapour permeability was determined by a standard method, according to HRN EN ISO 20344:2012. Samples of box calf leather and nappa leather, whose raw material is equal, were technologically processed in a similar manner (hydrophobisized, combination tanned and polyurethane finish of the face of the leather) have the highest water vapour resistance. In the case of identical processing a sample of less thick suede has lower water vapour resistance in relation to thicker suede. Water vapour permeability is largely dependent on the processing of the face of the leather. Suede samples have high values of water vapour permeability in comparison to samples of box calf and nappa leather, independent on thickness and processing which is associated with the permeable structure of their buffed face.

Keywords
Bovine leather, Water vapour permeability, Permetest, Professional footwear

1. Introduction

To determine parameters of thermo physiological comfort of footwear, different methods are used to measure two parameters, water vapour permeability (water vapour resistance) and thermal permeability (thermal resistance). In general, measurement methods of the mentioned thermo physiological parameters can be static and dynamic [1, 2].

One of the static methods for fabrics including leather is carried out by using a device called "Skin Model" (e.g. Hot plate) [3] and the other is implemented using a Peremtest device for the non-destructive measurement of samples [4]. Devices usually called “Thermal foot” (thermal mannequin, thermal leg) [5, 6, 7, 8) are used for dynamic measurements.

However, values of thermal resistance and water vapour resistance do not completely define footwear comfort. In addition to the objective parameters obtained by the above mentioned methods, it is necessary to carry out the examination of the comfort of the test subjects, which is longer.

Furthermore, in addition to activity levels, external conditions, footwear construction, material type (leather) for making footwear as well as its treatment to a great extent determine footwear comfort. The complexity of a more complete definition of footwear comfort is reflected in the fact that footwear is usually made from several layers, and the material and construction of the socks warn next to the skin together with the footwear should be considered too.

Further to the above-mentioned facts a more detailed description of the structure and technology of processing the leather for making professional footwear, which is the subject of the research in this paper, is given.

Finished leather for making footwear is obtained through the technological operation of processing raw animal hides. According to the histological structure of the skin there are three distinct layers:

- outer layer (epidermis, cuticle) accounts for 1 to 2% of skin thickness;
- medium layer (dermis, corium, cutis) accounting for 80 to 95% of skin thickness;
- inner layer (subcutaneous tissue, subcutis) making for 3 to 20% of skin thickness.

As far as leather processing is concerned, the most essential layer of raw hides for making finished leather is the medium layer (dermis). The dermis is made of solid, connective tissue of collagen fibres. Collagen fibres are made of fibrils - numerous parallel threads interlocked and intertwined in all directions without free ends. This structure is improved by processing, resulting in specific physical mechanical and chemical properties and the appearance of finished leather.

Rawhide processing consists of technological operations: preparatory stages, tanning process, finishing process of tanned hides and their various combinations. The preparatory stages are used to prepare raw hide for tanning. Tanning agents have the capability of true tanning, they have a different chemical structure and composition. Their mutual effect is to bond collagen fibres and to ensure their resistance to external influences with the aim of achieving a satisfactory durability of the finished leather. The fibre structure of the hide forms the basis for all the important properties of finished leather that depend on its microstructure, which includes the correctness of the fibre network, the angle of interlacing, fibre density, their bending, distribution degree and thickness.

Depending on the selection of tanning agents, vegetable, chrome and synthetic tanning agents are most commonly used as well as their different combinations. Chrome tanned leather has better physical-mechanical properties than vegetable tanned leather. Vegetable tanned leather compared to chrome tanned leather contains more bound tanning substances, unbound non-tanning substances, and it is heavier and contains thicker fibres. By use of synthetic tanning agents, specific properties of finished leather is achieved besides tanning action. In practice, a combination of chrome and vegetable tannage is frequent to achieve satisfactory properties of finished leather whereby more and more stringent safety and environmental requirements are met. By leather finishing operations important properties of the final leather appearance and suppleness, but also a variety of functional properties of finished leather, depending on the intended use, are achieved [9].

In addition to knowledge of the leather properties that are caused by types of raw material and technological processing, it is important to know the structure specificity of individual parts of the leather for its application in the production of professional footwear. For the production of footwear, it is necessary to know the specific properties of the croupon and belly and shoulder leather areas. The croupon area or the middle part of the leather has the best mechanical properties and is therefore most suitable for making shoe uppers. Collagen fibres are best structured in this part, i.e. they have the best microstructure properties.

The shoulder and belly part of the leather stretches more, is less structured, has less pronounced fullness, and it is more suitable for making uppers and less visible parts of the upper, such as tongue and collar. The fibre structure or fibre construction that determines the large internal reactive surface and is the basis for important physical properties of finished leather such as air, water vapour and thermal permeability. Leather has a specific microclimate that artificial materials try to achieve, such as the ability of retaining heat, air permeability, water vapour and moisture accumulation, which contributes to the so-called hygienic properties of footwear [9].

There are few published papers dealing with thermal resistance of the leather and even fewer papers dealing with the problem of water vapour permeability. Furthermore, a number of authors have been involved in thermal insulation of leather and footwear. Thus Kuklane [10] states that thermal insulation of the whole body affects the local heat, and local insulation, the insulation obtained by wearing shoes affects the overall thermal comfort of the human body. The accumulation of moisture in the leather significantly reduces footwear insulation.

A reduction in insulation depends on the rate of sweating, the evaporation-condensation rate, the absorption capacity of the footwear material and the moisture transfer in them. In the same paper, Kuklane specifies the values of thermal insulation of footwear (thermal resistance) for different ambient temperature conditions from +15 °C to -25 °C conditions. Krishnaraj et al. [11] investigate the thermal insulation of different leathers for making clothes of different designs and constructions. Çolak et al. [12] deal with thermal resistance of different leathers tanned with various tannages. Furthermore, Salopek Čubrić et al. [13] investigate comfort parameters (thermal resistance and water vapour resistance) of two different lining furs and one medical fur. Akalović et al. [14] investigate the influence of 11 different materials on the parameters of thermal and water vapour resistance (insole felt, double layer composite for the face, insole double layer composite, thermoplastic material for making stiffeners and sponge for making shoe collars).

The aim of this paper is to investigate how leathers (5 items) differently processed and physical properties for making professional footwear behave in terms of water vapour resistance/water vapour permeability as one of the basic parameters of footwear comfort assessment.

2. Experimental part

2.1. Materials

Important items of finished leather for making professional footwear are Box calf leather, Bovine suede, Bovine footwear suede, Bovine hydrophobised nappa and Footwear nappa.

Box calf leather is chrome tanned or combination tanned leather with naturally smooth or engraved face of leather. It was chrome tanned, slightly vegetable retanned and greased with combinations of synthetic and natural greases, and depending on usage it can also be differently hydrophobised. Raw materials are medium heavy cows. Depending on usage, different types of finishes (aniline, casein, and polymerisation) and combinations thereof are used.

Bovine suede leather is finished leather with buffed fleshy side, which is the face (outer side) of this type of finished leather. It is mostly chrome tanned or combination tanned, its colour is uniform and it is very soft and supple. It is dyed, greased with special combinations of greases which contribute to velvety appearance, and depending on usage it can be hydrophobised.

Bovine nappa is the leather of characteristic softness and suppleness with full natural face. It is usually chrome tanned and slightly retanned with vegetable or synthetic tanning agents and with the face finished with different finish types, and depending on usage, it can be hydrophobised.

For the purposes of the experiment, bovine leathers were chosen for making professional footwear, presented in Tab. 1. The Permetest was used to measure relative thermal permeability and water vapour resistance, while the results of their water vapour permeability and thickness were obtained from the domestic company and determined in compliance with existing standards [15, 16].

Sample A is box calf leather. It is black, hydrophobised, chrome tanned and slightly vegetable retanned. The face of the leather was finished with a PU finish. It is used to make headpieces, uppers, upper part of the tongue of the upper of the summer military ankle boot and the same parts of the winter military boot.

Table 1: Designations and description of tested samples

Sample label	Sample name	Technological Processes
A	Box calf leather	Hydrophobised, Chrome tanned Slightly vegetable retanned Face finished with PU finish
B	Bovine suede	Hydrophobised, Chrome tanned
C	Bovine footwear suede	Hydrophobised, Chrome tanned
D	Bovine hydrophobised nappa	Chrome tanned Slightly vegetable retanned PU finish of the face
E	Footwear nappa as lining leather	Chrome tanned

Sample B is hydrophobised bovine suede chrome tanned, beige coloured. It is used to make the collar of the summer military ankle boot.

Sample C is bovine footwear suede chrome tanned, hydrophobised in uniform sand colour and well coloured through the cross-section. It has good mechanical properties and satisfactory softness and suppleness; it is used to make the face of the upper of the summer military ankle boot.

Sample D is black hydrophobised bovine nappa to make collars for the upper of the summer military ankle boot as well as the collar and the bottom part of the tongue of the knee-high military boot and winter military boot. The leather was chrome tanned, slightly vegetable retanned, the face finished with PU finish.

Sample E is chrome tanned footwear nappa, which is in the professional footwear used as lining leather for the collar of the upper of the summer military ankle boot and summer sand coloured military ankle boots. It complies with functional properties of lining leather.

2.2. Test methods

2.2.1. Testing of water vapour permeability, according to HRN EN ISO 20344

Water vapour permeability tests of all five samples of the finished leather were conducted according to the valid standards [16]. The test specimen was placed on the measuring instrument (rotating tray with a hygroscopic substance placed in a strong airflow in the conditioned state: temp. 23 C ± 2, rel. humidity 50 % ± 5). Water vapour permeability results were expressed according to equation:

$$W_3 = \frac{M}{At} = \frac{M}{\pi r^2 t} \qquad (1)$$

Where is:

W_3 water vapour permeability in mg /(cm^2 × h),
M mass of water vapour (M_2 - M_1)/1000) in mg,
M_1 initial mass of the tray together with the test specimen and silica gel in g,
M_2 final mass of the tray together with the test specimen and silica gel in g,
A test area in cm^2,
r radius of the test area in cm,
t time between the first and second weighing in h.

2.2.2. Testing of water vapour permeability using the PERMETEST

Tests conducted on the Permetest device (Skin model, Fig. 1), which simulates dry and wet human skin [17], and the following parameters were measured:

a) relative thermal permeability (P) and
b) water vapour resistance (R_{et}).

Relative thermal permeability (P) is calculated by the following equation:

$$P = \frac{q_s}{q_o} \times 100 \qquad (2)$$

where is:

q_s thermal permeability with a specimen in W/m^2,
q_o thermal permeability without a specimen in W/m^2.

Water vapour resistance is calculated by the equation 1

$$R_{et} = (P_m - P_a)(q_s^{-1} - q_o^{-1}) \qquad (3)$$

Where is:

P_m partial pressure of the saturated water vapour of the ambient temperature of the room where tests are performed in Pa,
P_a partial pressure water vapour of the room/laboratory where tests are performed.

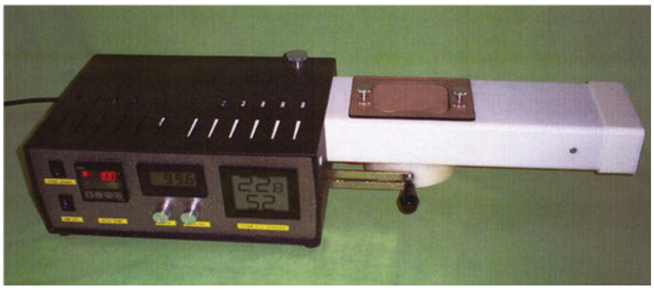

Figure 1: PERMETEST - device for non-destructive determination of water vapour and thermal resistance, by Sensora Instruments [17]

3. Results and discussion

Measurement results of water vapour permeability (by Equation 1), water vapour resistance (by Equation 3) and relative thermal permeability (by Equation 2) are shown in Tab. 2 and Figs. 2- 4.

Table 2: Measurement results of thermal resistance and water vapour permeability

Designation of sample	d (mm)	R_{et} (Pa m^2/W)	P (%)	W_3 (mg/(cm^2 h))
A_1	2,1 – 2,3	44,7	12,9	-
A_2	2,1 – 2,3	36,8	14,3	-
A_3	2,1 – 2,3	38,3	13,7	-
$\overline{x}$	**2,2**	**39,93**	**13,63**	**7,04**
σ	-	4,196	0,702	-
CV, %	-	10,50	5,10	-
B_1	0,9 – 1,1	9,5	39	-
B_2	0,9 – 1,1	8,8	40,7	-
B_3	0,9 – 1,1	8,5	42	-
$\overline{x}$	**1,0**	**8,93**	**40,57**	**15,30**
σ	-	0,513	1,504	-
CV, %	-	5,70	3,70	-
C_1	2,1 – 2,3	25,2	18,7	-
C_2	2,1 – 2,3	26,2	18,3	-
C_3	2,1–2,3	25,7	17,9	-
$\overline{x}$	**2,2**	**25,70**	**18,30**	**9,99**
σ	-	0,500	0,400	-
CV, %	-	1,90	2,20	-
D_1	1,8 – 2,0	55,6	9,8	-
D_2	1,8 – 2,0	38,7	13,6	-
D_3	1,8 – 2,0	54,2	10,3	-
$\overline{x}$	**1,9**	**49,50**	**11,23**	**5,54**
σ	-	9,379	2,065	-
CV, %	-	18,90	18,40	-
E_1	0,9 – 1,1	32,3	16,2	-
E_2	0,9 – 1,1	36,1	14,8	-
E_3	0,9 – 1,1	50,6	10,9	-
$\overline{x}$	**1,0**	**39,67**	**13,97**	**6,81**
σ	-	9,657	2,747	-
CV, %	-	24,4	19,7	-

d - Thickness (mm); R_{et} - water vapour resistance (Pa m^2/W); P - relative thermal permeability (%); W_3 - water vapour permeability (mg/(cm^2 h)); - mean value of tested properties; σ - standard deviation of tested properties; CV - coefficient of variation (%).

3.1. Water vapour resistance

Samples A (box calf) and D (bovine nappa) have a proportionally higher water vapour resistance (39.9 and 49.5 Pa m^2/W respectively, Tab. 2 and Fig. 2). Their raw materials are identical and they are technologically processed in a similar way (hydrophobised, combination tanned with polyurethane finish of the face.

Sample E (footwear nappa) has approximately equal water vapour resistance (39.7 Pa m^2/W) in relation to sample A (box calf) and slightly lower than sample D (bovine nappa). Sample E (footwear nappa) was not hydrophobised, chrome tanned, with PU finish of the face, so even in finishing it can searched for the cause of greater water vapour resistance.

Sample B (bovine suede) has relatively the lowest water vapour resistance (8.93 Pa m^2/W) and sample C (bovine footwear suede) has a slightly higher water vapour resistance (25.7 Pa m^2/W) compared to sample B (bovine suede).

By comparing the values of water vapour resistance of samples A (box calf) and C (bovine footwear suede) - leather for making the face of the uppers, the effect of processing on water vapour resistance is visible. Namely, sample C as suede has a lower water vapour resistance than box calf (sample A) which has PU finish of the face and combination tannage although their thickness is approximately equal (2.26 mm, 2.20 mm, Tab. 1).

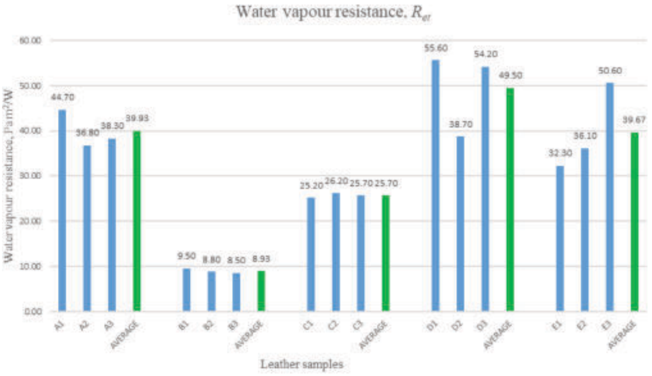

Figure 2: Water vapour resistance (R_{et}) of different leather samples for making professional footwear

3.2. Water vapour permeability

Water vapour permeability measured values of all five samples meet the prescribed requirements for military footwear. The highest value of water vapour permeability (15.30 mg / (cm^2 h), Tab. 2, Fig. 3) was measured in sample B and is consistent with its thickness of 1.09 mm and the structure of chrome tanned suede.

Sample C, suede for the face of the uppers had a slightly lower value of water vapour permeability amounting to 9.99 mg/(cm^2 h) in relation to sample B (bovine suede), which can be linked with the influence of leather thickness (Tab. 1).

Sample A, which is box calf, has a lower value of water vapour permeability amounting to 7.04 mg / (cm^2 h) than samples B (bovine suede) and C (bovine footwear suede), which is attributed to its structure. Sample A and sample C are leathers for the face of the ankle boot, having approximately equal thickness (2.20 mm, 2.26 mm, Table 1). The lower value of the water vapour permeability of box calf (sample A) can be explained by its structure of combination-tanned leather with PU finish. Vegetable tannage and PU finish of the face of box calf (sample A) produced a slightly lower value of water vapour permeability in relation to bovine footwear suede (sample C), besides chrome tannage, has an open suede structure of the face. On sample E of footwear nappa leather, chrome tanned, the value of water vapour permeability amounting to 6.81 mg / (cm^2 h) was measured and corresponds to the structure and permeability of lining leather, which was not hydrophobised.

By comparing the values of water vapour permeability of the samples E(footwear nappa) D (bovine nappa) it can be concluded that it is lower in sample D (5.54 mg/(cm^2 h), that can be explained with its combination tannage and PU finish of the face. In general, it can be concluded that the type of tannage and processing the face of the leather affect water vapour permeability property of finished leather and footwear comfort.

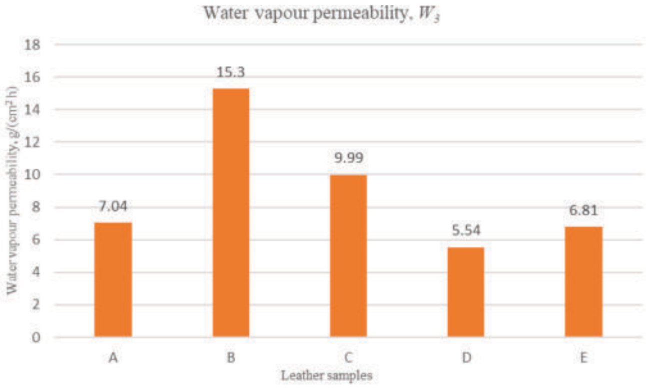

Figure 3: Water vapour permeability (W_3) of different leather samples for making professional footwear

3.3. Water vapour permeability and relative thermal permeability

By comparing the values of water vapour permeability and relative thermal permeability (according to 3), and by testing on the Permetest device the traceability of the obtained values is visible. When measuring water vapour resistance on sample B (bovine suede) which showed the highest water vapour permeability (15.3 g / (m2 × h), Tab. 2, Fig. 4) and the lowest water vapour resistance (8.93 Pa x m^2/W, Tab. 2, Fig. 2), a relative thermal permeability of 40.57% (Table 2, Fig. 4) was obtained in comparison with initial one to maintain dynamic equilibrium. By other words, the reduction of thermal permeability compared to the initial one, without a sample amounts to 60.57%. In sample C (bovine footwear suede) having lower water vapour permeability (9.99 g/(m^2 × h), i.e. higher water vapour resistance in comparison to sample B (bovine suede), relative thermal permeability of 18.3% was obtained or a reduction of 81.2% in relation to the initial reference measurement of thermal permeability for specific external ambient conditions.

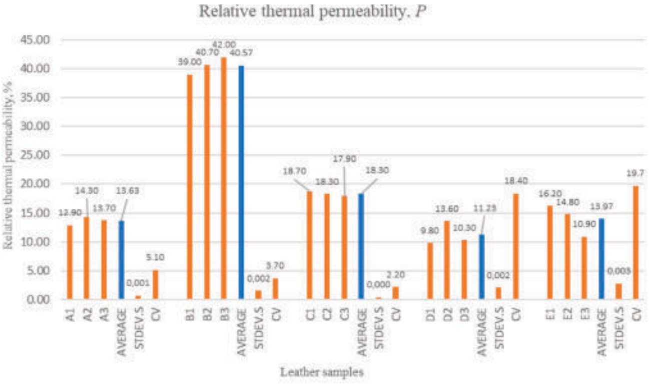

Figure 4: Relative thermal permeability (P) of different leather samples for making professional footwear

Hence, leather samples having higher water vapour permeability (lower resistance, e.g. sample B) need higher thermal energy on the Permetest device to achieve a dynamic equilibrium of water vapour permeability through a leather sample. The course of relative thermal permeability (Fig. 4) fully follows water vapour permeability or water vapour resistance for the tested leather samples (Figs. 2 and 3).

4. Conclusions

Based on the obtained values of water vapour resistance, relative thermal permeability and water vapour permeability the following conclusions can be drawn:

a) The samples of box calf and nappa leather whose raw material is identical, technologically processed in a similar manner (hydrophobised, combination tanned with PU tannage of the face of the leather) relatively have the highest water vapour resistance which is associated with the structure of the face of the natural leather processed with PU finish. The same can be concluded for the footwear nappa leather samples which were not hydrophobised and not combination tanned, but the face was PU finished; therefore, the values of water vapour resistance are approximate to the values of water vapour resistance of box calf and nappa leather.

b) The sample of the less thick suede has lower water vapour resistance in relation to the thicker suede in the case of identical processing.

c) Box calf has higher water vapour resistance in relation to footwear suede of approximately equal thickness and usage, which is associated with the differences in processing as well as with its structure, especially the structure of the face of the leather.

d) All the samples of PU finishes of the face of the leather (hydrophobised box calf and nappa, footwear nappa) have lower values of water vapour permeability independent of leather processing and its thickness; thus, it can be concluded that water vapour permeability depends on processing the face of the leather.

e) Suede samples have high values of water vapour permeability in relation to samples of box calf and nappa leather, independent on thickness and processing which is associated with the permeable structure of their buffed face.

Although all the samples of the tested leathers for making professional footwear meet normative requirements of water vapour permeability, a difference in water vapour permeability of the tested samples was obtained. The above-mentioned facts are significant for footwear designing and optimization of material selection, processing and construction of professional footwear. In general, it can be concluded that tannage type and processing the face of the leather affect properties of water vapour permeability of finished leather as well as footwear comfort.

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Acknowledgments

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