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Comparable Evaluation of Leather Waterproofing Behaviour upon Hide Quality. II. Influence of Finishing on Leather Properties

Virginija JANKAUSKAITĖ [1] *, Ada GULBINIENĖ [1], Indira JIYEMBETOVA [2], Justa ŠIRVAITYTĖ [3], Virginijus URBELIS [1], Kazys Vytautas MICKUS [1]

[1] *Department of Clothing and Polymer Products Technology, Faculty of Design and Technologies, Kaunas University of Technology, Studentų str. 56, LT-51424 Kaunas, Lithuania*
[2] *Department of Textile Products Technology, Institute of Technology and Information Systems, M Kh. Dulaty Taraz State University, Tolei bi str. 60, 080000 Taraz, Kazakhstan*
[3] *Department of Organic Technology, Faculty of Chemical Technology, Kaunas University of Technology, Radvilėnų str. 1, LT-50254 Kaunas, Lithuania*

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Unfinished leather has high water vapour permeability and low waterproofness because of its natural porous structure. To modify the surface appearance and hide any defects, to improve physical properties, such as light and rub fastness, resistance to water, solvents, abrasion, etc., leather needs to be finished. In this study the influence of waterborne finishing agents on the waterproofness and breathability of the hydrophobic leather obtained using different retanning, waterproofing, neutralization and dispersing agents has been investigated. The leather was characterized using morphological analysis and permeability studies.

Keywords: leather, finishing, polymer coat, breathability, waterproofness.

1. INTRODUCTION

Various types of footwear have been developed considering different conditions of life and work. There are significant differences between shoes used in our daily life and those manufactured for industrial, agricultural, military, athletic and artistic purposes. Nevertheless, it is widely recognized that all shoes must be water vapour permeable, or breathable, and comfortable. The breathability allows perspiration to evaporate promptly when activity level increases; therewith the heat generated by metabolism can be continuously dissipated and regulated, guarding against a damp and roasted feeling [1, 2]. On the other hand, shoes, especially these for industrial and military purposes, must protect foot from wet and cold environment.

Leather is most commonly used in shoe manufacturing, because it demonstrates positive results regarding foot health and comfort [3, 4]. The comfort created by leather can be explained by leather structural peculiarities together with its exclusive physical and chemical properties. Water vapour permeability and water absorption properties of leather are of great significance [5]. Leather shows high level water vapour permeability as well as ability to absorb the dampness inside the shoes. Meanwhile, processing of waterproof leather requires a special selection of wet-blue, special products – waterproofing agents and selected retanning, neutralization and dispersing agents – and special application. In previous study [6] was shown that properly selected retanning and fatliquoring agents and their compositions with properly harmonized properties, also sufficient selected methods of such compositions application allow to produce hydrophobic leather with the desired properties even from the hide of low quality.

It is possible that leather finishing technology can influence on water vapour permeability and water repellency. Unfinished leather has high water vapour permeability and low waterproofness because of its natural porous structure. To modify the shade, gloss, handle, to improve its physical properties, such as light and rub fastness, resistance to water, solvents, abrasion, etc., and hide any defects or irregular appearance, leather needs to be finished [7, 8]. It is determined that water vapour permeability of polyurethane finished leather decreases 30 % – 50 % compared with the unfinished one [9, 10]. Yet more water vapor permeability decreases in the case of leather lamination [11].

Three families of polymeric binders are used in leather finishing: acrylic, polyurethane and butadiene. Each of them has specific characteristics according to their base monomer, polymerization degree, molecular weight, type of functional groups in their side chains, and number of intramolecular and intermolecular bonds [8].

The main characteristics of butadiene binders are their rubber-like behaviour, high binder power, flexibility (even at low temperature), and filling properties [12]. However, they are sensible against autoxidation, lead sometimes to difficulties with adhesion [8].

Polyacrylates are the most used polymers for leather finishing [13 – 15]. They show good adhesion and compatibility with many additives, possess high stability against shearing. Disadvantages are their sensitivity to organic solvents, not good mechanical strength and finally high thermoplasticity [8].

Currently, polyurethane (PU) is widely employed as coating-forming material for finishing of leather due to the good film-forming performance and adhesion, simple production process and low production cost [10, 16 – 18].

*Corresponding author. Tel.:+370-37-300207, fax: +370-37-353989, E-mail address: *virginija.jankauskaite@ktu.lt* (V. Jankauskaitė)

The properties of PU are remarkably affected by the content, chemical structure, and molecular weight of soft segments [19, 20]. It is well known that ester-type polyol-based PU provides better mechanical properties, whereas the ether-type polyol-based PU shows better hydrolysis, softness, and water vapour permeation properties.

To obtain double benefits to the environment/economy, waterborne finishing agents have been widely applied in leather finishing [15, 17 – 20]. Aqueous binder compositions have advantages in environmental pollution, fire safety, and soil resistance compared to solvent based one. To enhance breathability of such coatings the modification with nanoparticles often are proposed [21, 22].

The initial quality of skin or hide has also significant influence on the waterproofness and breathability of finished leather [6]. Therefore, in this study the influence of waterborne finishing on the waterproofness and breathability of the hydrophobic leather obtained using different retanning and fatliquoring agents has been investigated.

2. EXPERIMENTAL

2.1. Materials

Hydrophobic leathers obtained according to the different chrome tanning technologies in JSC "Natūrali oda", Lithuania (NO) and company "TarazKozhObuv", Kazakhstan (TKO) were investigated. The chrome-tanning technologies to be used are particularly described in [6]. Three types of grain surface leathers (TKO-1uF, TKO-2uF, NO-2uF) and three types of polymer coated (TKO-1F, TKO-2F, NO-2F) – were chosen for investigation of the finishing influence on the leather resistance to the water penetration and breathability.

Structure of finishing applied in this study is presented in Fig. 1. Spray staining was used to level drum dyed shades, while grain impregnation – to tighten the grain and impart a settled appearance and smoothness of the surface. These operations were used for all unfinished grain surface leathers and finished one. Previous it was determined that grain impregnation do not influenced on the leather breathability, but decreases water uptake [23].

To ensure good adhesion to the finish coat adhesive coat consisting of pigments, binders and auxiliaries was applied. The pigmented base coat imparts the desired appearance to leather and levels out the surface. It is usually harder than adhesive coat. Eventually the top coat determines the final appearance and the handle of the leather surface and has a decisive influence on the fastness properties of the finish.

Coating formulations applied for leather of different tanners are listed in Tables 1 and 2. Company "TarazKozhObuv" for leather finishing used chemicals produced by corporation "VneshChimOpt" (Russia), while JSC "Natūrali oda" – by "Stahl Europe" (Netherlands).

In both cases base coating was applied using air spraying (50 g/m^2), with plating after second application at 100 °C temperature and 75 bar pressure. In all cases leathers were coated with pigmented water-based acrylic emulsions and aliphatic polyurethane dispersion. In the case of leather NO-2 approx. 72 % aqueous acrylic/polyurethane binder composition was used, while leathers TKO were coated with binder composition of lower concentrations (ca. 58 %). However, in this case more layers were sprayed on the leather surface (3 layers).

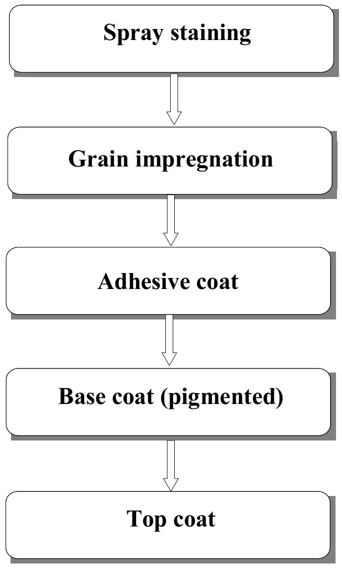


Fig. 1. Processes of leather finishing

Table 1. Coating formulations for leathers TKO-1F and TKO-2F

Adhesive coat / Base coats (3 layers)	
100	Pigment
50 – 70	Wax
500	Acrylic/polyurethane binder
50	Penetrating agent (nonionic surfactant)
500	Water
Top coat	
100	Nitrocellulose lacquer
5	Silicone
100	Water

Table 2. Coating formulations for leather NO-2F

Adhesive coat	
100	Polyurethane binder
400	Water
50	Isopropyl alcohol
Base coats (2 layers)	
100	Pigment
500	Acrylic binder
200	Polyurethane binder
300	Water
Top coat	
450	Polyurethane lacquer
30	Polyaziridine crosslinker
5	Silicone
530	Water

The base coated crust were then sprayed with top coat (40 g/m^2) and subsequently pressed. For leathers TKO-1F and TKO-2F aqueous nitrocellulose emulsion was used, while leather NO-2F was sprayed with dull and high gloss polyurethane dispersions blend as cross-linker using aziridine. Although aziridine is harmful to humans, but it is effective mean to improve wet rub fastness of leather [8].

2.2. Testing

Before physical testing all leather samples were conditioned at standard atmosphere in accordance with the requirements of LST EN 12222 at a constant temperature $T = 23$ °C ±2 °C and relative humidity $RH = 50$ % ±5 %.

Leather chemical analyses – chromium content, the matter soluble in dichloromethane and volatile matters, i. e. moisture – were determined according to the methods briefly described in [6].

Leather permeability properties (water penetration at dynamic conditions and water vapour permeability, water vapour absorption, water vapour coefficient) were performed according to the requirements of standard methods [6].

SEM analysis of leather structure was performed using microscope Quanta 200 FEG (FEI, Netherlands). All microscopic images were done at magnification 200× on the same technical and technological conditions [6].

3. RESULTS AND DISCUSSION

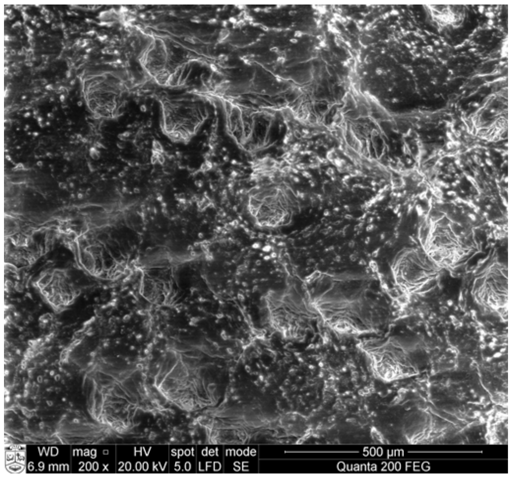
The chemical materials defined in investigated unfinished and finished leathers are presented in Table 3. As can be seen, leather finishing do not influences on the amount of chemicals.

Table 3. Chemicals content in leathers to be investigated

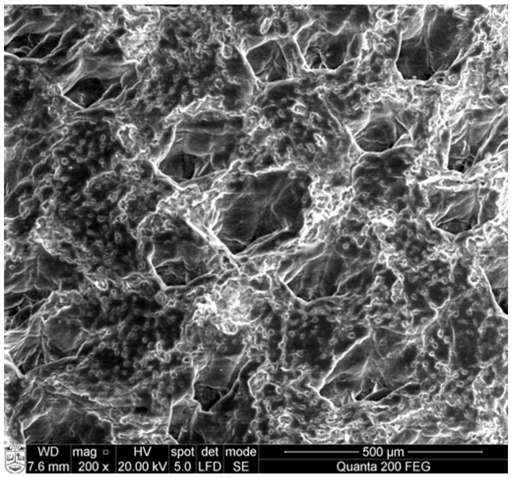
Leather type		Content of chemical materials in leather, %:		
		chromic oxide	matter soluble in dichloromethane	volatile matter
Unfinished	TKO-1uF	4.80	3.62	13.02
	TKO-2uF	5.02	6.79	13.50
	NO-2uF	4.56	3.34	11.24
Finished	TKO-1F	5.09	3.82	12.39
	TKO-2F	4.48	6.71	13.00
	NO-2F	4.43	2.84	11.43

In all unfinished (crust leather) and finished leathers chromium and moisture contents have close values (4.5 % – 5.0 % and 11 % – 13 %, respectively). However, the matter soluble in dichloromethane (fatty substances) depends on the complex chemical processing of the wet-blue involving retanning, dyeing and fatliquoring. As was supposed in [6], TKO-2 leathers have twice higher fatty substances content due to the fatliquoring process in the separate stage at elevated temperature.

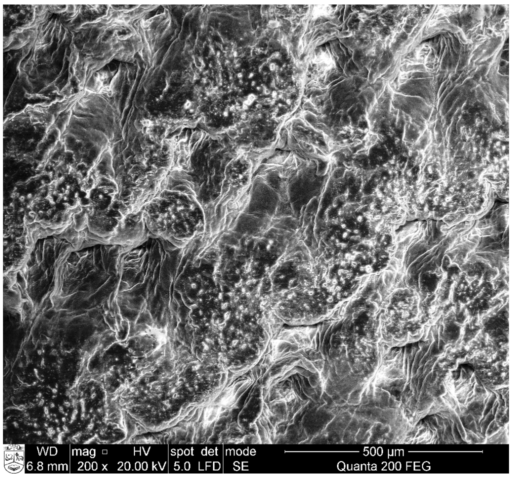
The SEM images of crust leather showing grain surface at magnification of 200× are given in Fig. 2. It is seen that grain structure of the samples is fibrous, clean without any damage. The hair pores are clearly visible without any surface deposition of tanning agents. However, the appearance of the fibres is related to the leather processing, through which it had passes [24, 25]. For leathers TKO-1uF and NO-2uF the coatings appear less fibrous and are more robust than in the case of the leather TKO-2uF. Besides, the hair pores of leather TKO-2uF are markedly large (about 100 μm – 150 μm in diameter), while microstructure of leathers TKO-1uF and NO-2uF are more dense and homogeneous in morphology.



TKO-1uF



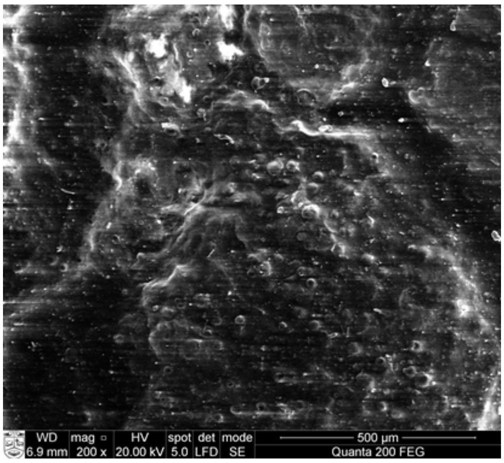
TKO-2uF



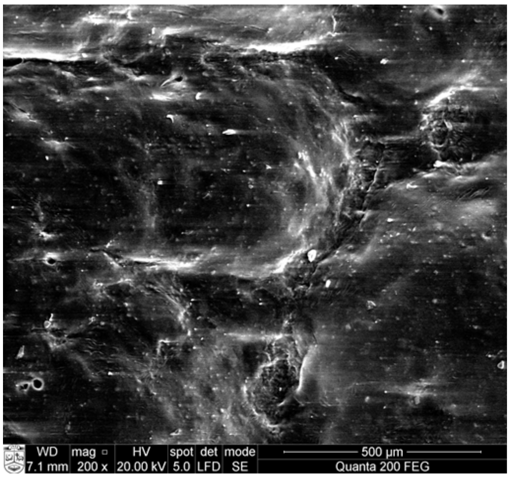
NO-2uF

Fig. 2. SEM images of chrome-tanned crust leather showing the grain surface (magnification 200×)

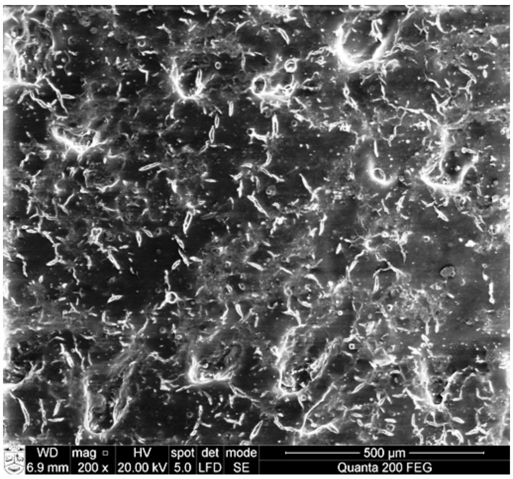
The SEM images of polymer coated leather surface are presented in Fig. 3. It is visible that surfaces of leathers TKO-1F and TKO-2F have embossed finish and are covered with monolithic polymer film.



TKO-1F



TKO-2F

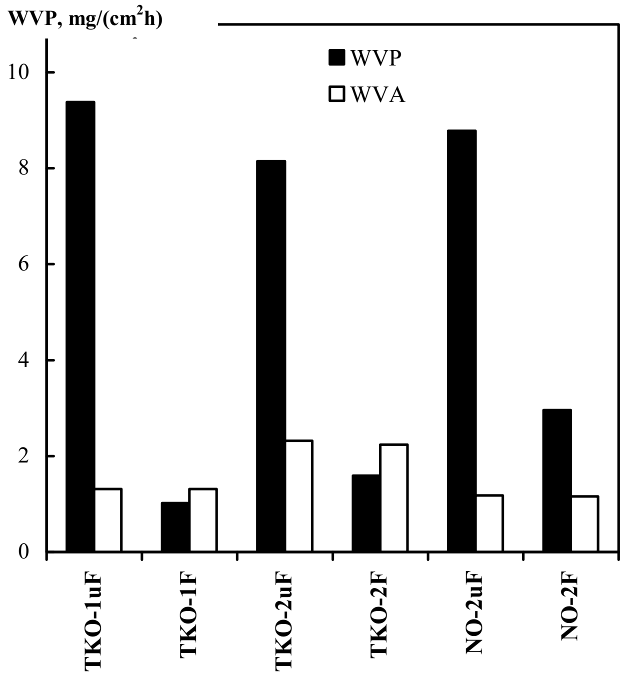


NO-2F

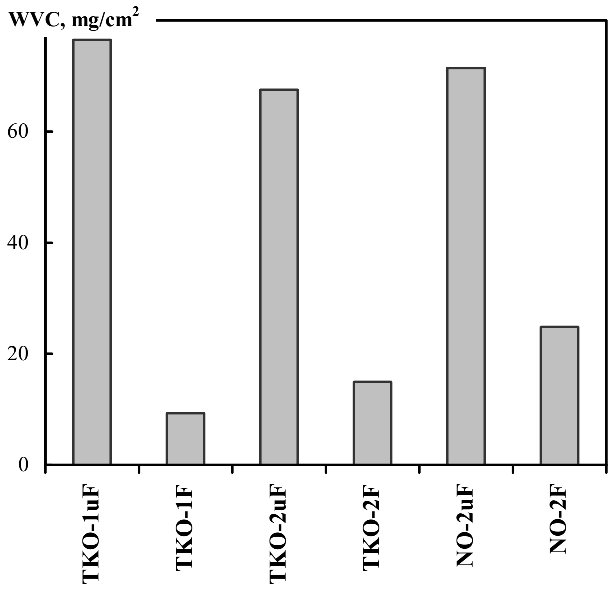
Fig. 3. SEM images of chrome-tanned polymer coated leather surfaces (magnification 200×)

Meanwhile, appearance of the polymer coated leather NO-2F surface is very similar to that of unfinished (see Fig. 2). Its surface after finishing retains the fibrous nature, which, as may be supposed, influences on the high water vapour permeability [6].

The investigations of breathability confirm differences in the leather surface morphology upon finishing (Fig. 4). As can be seen from Fig. 4, a, water vapour permeability (WVP) of unfinished leathers TKO-1uF and TKO-2uF is in 5 – 9 times higher compared to that of finished one (TKO-1F and TKO-2F) due to the formation of impermeable coating layer. Meanwhile, the polymer coating of leather NO-2F surface decreases the water vapour permeation ability only 3 times. It may be explained by significantly higher surface hydrophilicity of acrylic/polyurethane coating of leather NO-2F that plays important role in allowing water vapour permeation, since hydrophilic polyurethane groups facilitate the sorption of water vapour molecules on to the coating surface [26].



a



b

Fig. 4. Dependence of breathability upon leather finishing level: WVP – water vapour permeability; WVA – water vapour absorption; WVC – water vapour coefficient

Water vapour molecules permeate through dense hydrophilic coating by sorption-diffusion-desorption mechanism [27]. On the other hand, WVP of unfinished leathers almost do not depends on the leather type and get close values in the range of (8.2 – 9.4) mg/(cm^2·h).

However, leather polymer finishing do not influences on the water vapour absorption (WVA). It values before and after leather finishing remains the same. As was shown early [6], WVA only slightly depends on the hydrophobic leather processing technology, because after water repellent treatment interfacial tension between leather fibres and water increases that almost eliminates their interaction.

Unfinished leathers have significantly higher water vapour coefficient (WVC) values, since it depends on the WVP and WVA values [6]. From Fig. 4, b, it is evident that in the case of unfinished leathers WVC 4.5 – 5 times exceeds required value (67 – 76 mg/cm^2 compared to that of 15 mg/cm^2). But after polymer coat formation WVC decreases significantly and only in the case of leathers NO-2F and TKO-2F its value satisfies required one.

Dependence of finishing influence on the leather water absorption (WA) at dynamic conditions is shown in Fig. 5. The finishing has only negligible influence on the water uptake at first testing stage, i. e. after 1 h of testing. In this case absolute differences between WA values of unfinished and finished leathers reach only 1.0 % – 2.5 %.

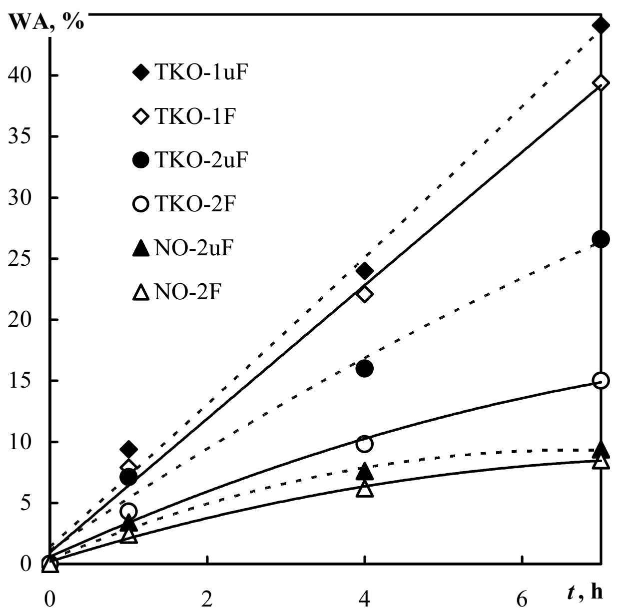


Fig. 5. Dependence of water absorption of grain surface (– – – –) and polymer finished (———) leathers upon their type at dynamic testing

However, further increase of testing time up to 7 h shows significant changes of water uptake for all types of leathers. It is clear visible that low packing density leather TKO-1 even coated with monolithic impermeable polymer layer shows low water resistance properties. Polymer finish decreases leather WA value only in 12 %. Also the same results were obtained in the case of NO-2 leathers, when breathable polymer coat increases water resistance in 10.5 %. Such results let to propose that the resistance to water penetration mainly depends on the leather structure density and water repellency properties assumed after retanning and fatliquoring. On the other hand, as follows from the results obtained with leather TKO-2, some resistance to the water penetration can be increased by leather polymer finishing. In this case impermeable finishing decreases water absorption in 77 % (from 26.6 % down to 15 %). However, the breathability of such leather decreases also markedly (see Fig. 4 ,a).

4. CONCLUSIONS

Leather aqueous acrylic/polyurethane polymer finish decrease water vapour permeability, but do not influence on the water vapour absorption properties. Degree of water vapour permeability changes depends on the leather coating nature. Dense hydrophilic coating has less influence on the breathability, because water vapour molecules can permeate by sorption-diffusion-desorption mechanism through the coating layer.

Water uptake mainly depends on the leather fibrils bundles packing density, influenced by leather quality and retanning and fatliquoring chemical materials and their application procedure. Monolithic impermeable polymer coat can increase leather resistance to water penetration, but breathability of such leather markedly decreases.

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