ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 18, No. 2. 2012

Comparable Evaluation of Leather Waterproofing Behaviour upon Hide Quality. I. Influence of Retanning and Fatliqouring Agents on Leather Structure and Properties

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crossref http://dx.doi.org/10.5755/j01.ms.18.2.1918

Received 30 December 2011; accepted 24 April 2012

For military leather processing pinnacle technologies are applied, because the leather must have extreme hydrophobicity, herewith to maintain the breathability and moisture management capabilities. Therefore, leather producers must use such tanning chemicals, which are able to impart sufficient waterproofness and vapour permeability. In this study the influence of retanning and fatliquoring technologies for wet-blue hide conversion into finished military leather on its waterproofing behaviour and breathability has been studied. The comparable evaluation of leathers manufactured in Lithuanian and Kazakhstan tanneries was carried out. The leathers were characterized by chemical analysis and moisture absorption, water vapour permeability and water vapour absorption properties.

Keywords: military leather, retanning and fatliqouring technologies, waterproofness, breathability.

1. INTRODUCTION

Water resistance of leather is an important property to several applications, like footwear and clothing with high wearing comfort even under wet and cold conditions. Furthermore, leather, which has absorbed too much water, loses its ability to insulate against heat and cold [1]. Therefore, waterproof leather used for footwear should not uptake more than 25 % – 30 % of water [2]. However, the leather should allow additionally high water vapour permeability and some reversible water up-take to remove perspiration from body.

To understand how to prevent the wetting of leather, it is necessary to understand the process of leather wetting. Generally, it takes place in four-steps [2]:

– water spreads over and wets the leather surface;

– water penetrates into the leather;

– water wets the fibre network (i. e. internal surface of leather);

– the leather soaks by water due to the attractive interaction between water and leather. Not only collagen backbone, but also tanning agents, dye molecules, salts, and other materials which present in leather network, might be involved in these interactions.

There are many polar functional groups in collagen fibres such as –OH, –COOH, $–NH_2$ and –CONH–. The chemical compounds to be added mostly are hydrophilic and have good water affinity. Therefore, to improve water resistance property several leather making processes and leather surface modifications are applied [2 – 4]:

1. Sealing the leather with an impermeable layer, i. e. a heavy polymer finish. A foil or thin laminate of waterproof synthetic material can be attached to the surface of the leather by adhesive, also [5]. The spreading of water over the surface is prevented by film and the leather cannot be wetted at least under static conditions. However, such film reduces the water vapour permeability drastically even produced using most modern technologies [5, 6].

2. Closed waterproofing – closing the spaces between the leather fibres with water-repellent substances [3, 4]. It might be achieved in two different ways: firstly, leather impregnation by incorporation of water-insoluble substances, for example, solid fats, and molten waxes; secondly, using hydrophilic waterproofing [7]. Grease impregnation is a long established system, and gives a special look and feel to the leather. However, the filling of the gaps with grease prevents the penetration of water into the fibre network, but the leather becomes extremely heavy and completely blocks any air and water vapour permeability. In the second case waterproofing of leather is achieved by application of certain surfactants (e. g. hydroxycarboxylic acid derivatives, alkenyl-succinic acid derivatives, hydroxyethylation fatty acid, etc.), which bind to the leather and can absorb a certain quantity of water [8]. The surfactants and water form highly viscous water-in-oil emulsion, which fill the gaps in the fibre network. These micelles are hydrophobic on their outer side and, therefore, the gaps are filled with a hydrophobic material. The problem with closed waterproofing is that it (partially) seals the pores and, therefore, frequently impairs the water vapour permeability and water vapour absorption of the leather [2, 3].

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3. Open waterproofing – creating a hydrophobic net around the fibres without filling spaces – is smartest approach to make waterproof leather [2 – 4]. Used low surface energy (not higher than 30 mN/m) waterproof agent binds to the fibres and fibrils through its functional groups and forms hydrophobic layer. Water vapour can penetrate into the fibre network, while water droplets possess high surface tension and cannot spread over the hydrophilic fibre and wet the internal surface. High interaction between fibre and waterproof agent is required. It can be realized by using chrome stearates, which consist of hydrophilic and hydrophobic parts, hydrophobic esters and silicone based products.

There are many other factors that influence the waterproofness of leather not only chemical substances used in leather manufacture (salts, tensides, tanning agents, retanning agents, dyestuffs, fatliquoring agents and finishing agents). The initial quality of skin or hide and operation of each process of the skin/hide conversion to the finished leather have significant influence on the waterproofness degree of finished leather [9, 10].

The problems that affect leather quality begin when the animal is still alive, and include, cuts resulted by barbed wire; in-fighting among male members and thorn scratches and cuts; brand marks made for ownership purposes using hot iron; holes and spots from infections and infestations, caused by ticks, horn flies, mange and bot-flies, among others; abscesses resulted from wrong vaccination techniques and natural growth marks or excess weight related problems, like furrows and wrinkles [9]. During transportation, the animal skin may suffer deep injures from nails and wood splints in the truck.

Before tanning, three important processes, which can also cause leather damage, happen: bleeding, skinning and curing. Insufficient bleeding can cause vain marks, while wrong skinning techniques may result in flaying cuts that, in some cases, may turn unusable otherwise valuable parts of the leather. As the raw hide is subjected to putrefaction, as soon as the animal dies, the raw hide must be cured to protect it until the tanning process begins, and this time can take months. Improper curing may lead to rotting and putrefaction. The defects during tanning and post-processing are much less common, as they are controlled by the tanneries, which have in the leather quality their main business [9].

Waterproof leathers are commercially of high interest because this leathers are sold at a relative high price due to requirement of specialty products for tanning (waterproofing, selected retanning, neutralization and dispersing agents) [2]. The choice of waterproofing system depends on the degree of water resistance required, the purpose of leather, and price. Extreme hydrophobicity is required for military footwear leather [11]. On the other hand, attention must be paid to the breathability and rate of drying out of leather. Therefore, for military leathers pinnacle technologies can be applied.

The aim of this work was to evaluate the waterproofing behaviour of the military leather upon various combinations of retannage and fatliquoring agents. The influence of hide quality on the military leather water resistance and breathability were evaluated as well.

2. CHOISE OF RETANNING, FATLIQUORING AND FILLING CHEMICALS

The skins and hides tanning with chromium salts induces the collagen fibre to be resistant against bacterial attack and increase resistance to temperature. However, this process does not possess the physical and aesthetic properties required to the products made from leather. Therefore, after chrome tanning obtained wet blue is converted to usable leather in a series of chemical and mechanical operations (i. e. retanning, fatliquoring, etc.) [1].

The highly complex chemical processing of the wet blue involving retanning, dyeing and fatliquoring (RDF) are used for manufacturing of leathers (Fig. 1). RDF process commences with the neutralization, when pH is raised to over 4.8 on purpose to provide even penetration of subsequent chemicals into the leather [1, 8].

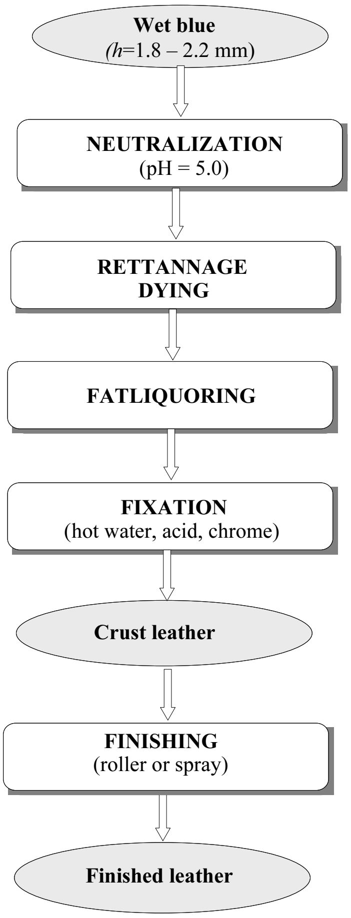


Fig. 1. Succession of chemical processes in the conversion of wet blue to dyed crust and the finished leather

The choice of retanning and fatliquoring chemicals depends on the desired properties (softness, touch, fullness, grain firmness or looseness, smell, adhesion properties, water uptake or release, and water repellency) of the final leather.

Various retanning agents were developed to give the chrome tanned leather fullness with selective filling of the structure and to provide tight and uniform grain surface [8, 12 – 14]. In general, retanning agents can be inorganic mineral substances (chrome, aluminium, zirconium salts) or organic materials (vegetable or synthetic). The synthetic retanning organic agents can be divided into three main groups: 1) syntans (condensation products of aromatic compounds like phenol, naphthalene sulphonic acid with formaldehyde or urea); 2) resins (condensation products from formaldehyde with amino and amido compounds like urea, melamine, and dicyandiamide); 3) polymers, mainly acrylic (polymerization products from acrylic acid derivatives). Syntans are better soluble in water than vegetable tannins, because they molecules are smaller. Therefore, vegetable tannins more difficult penetrate to leather matrix, and leather tanning process runs longer [1, 8]. However, vegetable tans can reduce or prevent the formation of harmful Cr(VI), promote antioxidation properties, improve burnishability and glazing, fix cationic dyes [15].

The wide use of acrylic acid derivatives is related to the presence of many carboxylic acid side groups that can give tanning property both reacting with multiple chrome centers on the leather and chemical bounding to the collagen groups [12]. Acrylic resin interaction mechanism with chrome tanned leather is presented in Fig. 2 [7].

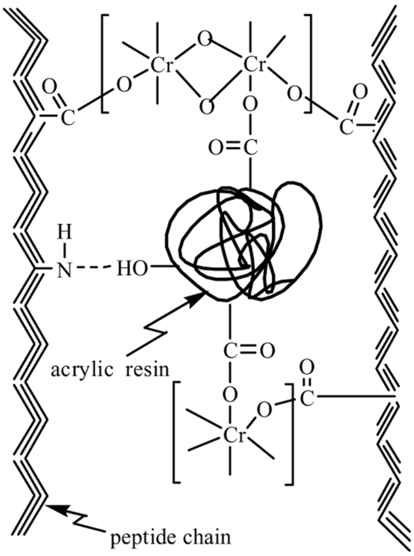


Fig. 2. Interaction of acrylic resin with peptide chain and chromium [7]

Synthetic retanning materials also are used for filling and softening, as auxiliaries during fatliquoring and sometimes as replacements of tannins in combination with vegetable extracts [12]. The filling improves the tightness and fineness of the leather grain with mellow surface.

The retanning agents play important role in the final degree of leather water repellency, also. Melamine-dicyandiamide resin, acrylo-nitrile resin, styrene-maleic copolymer, chestnut can significantly to lower water absorption of leather [16].

In recent, many researches are focused on the leather properties (such as reduction of water uptake) modification by grafting to collagen of different monomers such as styrene and acrylate derivatives [17, 18].

Fatliquoring agents are one of the important leather chemicals that have great effect on leather performance. It can penetrate into the interwoven structure of the collagen fibres, prevent the leather fibers from putrefaction, make the fibres stick together and improve their physical and mechanical capabilities [7, 8, 19]. The fatliquoring is the main step in the production of hydrophobic leather [7, 14, 16].

Generally, fatliquoring substances are divided into hydrophobic (emulsified) components and hydrophilic (emulsifying) components [1, 8]. In the last decades several products have been applied to impart waterproofing properties of the leather [14, 16, 20 – 22]: natural oils, alkenyl succinic acids, polysiloxanes, chromium soaps (stearates and oleates), phosphoric esters and reactive agents or amphiphilic polymers.

Multifunction fatliquoring agents can offer more new capabilities for leather. Besides fatliquoring function, they can enhance segment mobility of molecular chain of collagen fibers, and contribute higher level of softness, flexibility, waterproofness, perspiration resistance, etc. [20, 21]. Not only waterproofing but also repellent properties to the leather confer silicone derivatives and fluorcarbonated resin [2, 4]. Silicones may be applied from hydro-carbon solvents on the dry leather by dipping or spraying or a silicone emulsion may be applied in the drum on the wet leather by a fatliquoring [23, 24]. Silicones have very high interfacial tensions relative to water and these are not very temperature sensitive. However, silicones are not very effective as solo agents [1]. Fluorocarbons are applied from solvent solutions and have equally high water repellency and also oil repellency [25].

3. EXPERIMENTAL

3.1. Materials

For comparable evaluation the hydrophobic leathers tanned with different type of retanning and fatliquoring agents in JSC “Natūrali oda & Ko” (Kėdainiai, Lithuania) and “TarazKozhObuv” company (Taraz, Kazakhstan) were chosen. Characterization of fully finished leathers to be investigated is presented in Table 1. As can be seen, NO-type leathers are stiffer compared to that of TKO-type one.

Table 1. Characterization of hydrophobic leathers to be used for investigations

Leather producer	Chemicals suppliers	Type	Sample	Thickness, mm	Stiffness, N
Natūrali oda & Ko (Kėdainiai, Lithuania)	*Schill+ Seilacher* (Germany) / *Stahl International* (Netherlands)	Black	NO-1	2.2 ±0.1	3.5
	Schill+ Seilacher (Germany) / *BASF Group* (Germany) / *Stahl International* (Netherlands)	Brown	NO-2	2.1 ±0.1	2.7
TarazKozhObuv (Taraz, Kazahstan)	*Smit & Zoon* (Holand) / *Hayana Leather Chemicals* (Spain)	Black, with embossed surface	TKO-1	2.0 ±0.1	2.3
	Smit & Zoon (Holand)/ *Shelkovo Agroxim* (Russia)	Black, with embossed surface	TKO-2	1.9 ±0.1	2.4

Table 2. Chemical materials used in the RDF processing to obtain waterproof leather

RDF process stage	Chemicals used for RDF of leather			
	NO-1	NO-2	TKO-1	TKO-2
Washing thoroughly at T = 35 °C–40 °C, drain float				
I. Neutralization	Sodium formate Sodium bicarbonate	Sodium formate Sodium bicarbonate	Sodium formate Sodium bicarbonate	Sodium formate Sodium bicarbonate
Retanning	Phenolic compound (*Ukatan NR*) Maleic acid styrene copolymer ammonium salt (*Derugan NG*) Sodium salt of an amine modified fatty acids (*Limanol PEW*)	Aqueous anionic acrylic polymer solution (*Densotan A*) Maleic acid styrene copolymer ammonium salt (*Derugan NG*) Dicyandiamide resin (*Ukatan AG*)	Aqueous polyacrylic dispersion for retanning (*Retan 38*)	Aqueous acrylic polymer (*Syntan RS 3*)
Drain float, washing thoroughly at T = 25 °C–30 °C				
II. Retanning	Dicyandiamide resin (*Ukatan AG*) Maleic acid styrene copolymer ammonium salt (*Derugan NG*)	Dicyandiamide resin (*Ukatan AG*) Maleic acid styrene copolymer ammonium salt (*Derugan NG*)	Aqueous acrylic polymer (*Syntan RS 3*) Mixture of lignin sulphonate and phenolic sulphonic acid condensate (*Syntan GP*) Emulsified synthetic oils (*Synthol EW 321*) Aqueous solution of acrylic acid and ester copolymer (*Syncotan TL*)	Mixture of lignin sulphonate and phenolic sulphonic acid condensate (*Syntan GP*) Aqueous acrylic polymer (*Syntan RS 3*)
Filling	Protein filling agent (*Synektan F*) Chestnut	Polyphenol copolymerized with acrylic monomer (*Synektan R-982*) Chestnut	Melamine-urea-formaldehyde condensate (*Syntan LF 187*) Dicyandiamide-urea-formaldehyde condensate (*Syntan DF 585*)	Melamine-urea-formaldehyde condensate (*Syntan LF 187*) Dicyandiamide-urea-formaldehyde condensate (*Syntan DF 585*) Quebracho
				III. Washing at T = 40 °C
Fatliquoring (water repellants)	High molecular weight paraffines and hydrophobic emulsifiers (*Perfektol HQ*) Polymers combined with highly effective silicone-based additives (*Perfektol QX*) Unsaturated marine oil (*Perpristol COD*)	High molecular weight paraffines and hydrophobic emulsifiers (*Perfektol HQ*) Silicone based water repellent (*Densodrin EP*) Aqueous anionic acrylic polymer solution (*Densotan A*)	Emulsified synthetic oils (*Synthol EW 321*) Aqueous solution of acrylic acid and ester copolymer (*Syncotan TL*)	Emulsified synthetic oils (*Synthol EW 321*) Concentrated anionic agent (*Paste VNIZ*)
Drain float, twice washing thoroughly at T = 40 °C (first) and T = 20 °C–22 °C (second)				

JSC "Natūrali oda & Ko" as a raw material for leather manufacturing used local salted cattle hide not only high quality, but second-rate as well. For the processing of military leather with high waterproofness only top-quality wet-blue hides were chosen.

"TarazKozhObuv" company for manufacturing of military hydrophobic leather used only low quality skin and hide. Overall, purely 1 % – 5 % of Kazakhstan skins/hides are second-rate. Wet blue produced from third-rate (35 % – 45 %) is realized to China. The main part of skins/hides (50 % – 60 %) is fourth-rate and only this raw are used for the military leather manufacturing. Such low quality of Kazakhstan skins and hides is related to the insufficient structure evenness due to the intensive cattle growth, various diseases of cattle, holes or spots obtained from infections and infestations. Many injures are obtained during bleeding, skinning, and curing.

3.2. Applied chemical processes of conversion wet-blue to finished leather

Wet-blue hides shaved to 1.9 mm – 2.2 mm were tanned according to the conventional technology (Fig. 1). Neutralization, retanning, filling and fatliquoring operations applied for leather manufacture to produce waterproof leather are presented in Table 2. In all chemical processing cases the neutralization is followed at (35 – 40) °C temperature using sodium formate and sodium bicarbonate. During the neutralization the pH of leather processing medium changed from 3.2 – 3.4 to 4.8 – 5.4.

As neutralization and retanning processes proceed simultaneously, NO-type leathers additionally were neutralized by retanning chemicals based on phenolic compounds (*Ukatan NR*) and anionic acrylic polymer solution (*Densotan A*). When pH is higher than 4.0, acrylic compound *Syntan RS 3* also acts as neutralization agent (TKO-2 leather).

For the studied leathers the retanning both aromatic (phenolic agents) and aliphatic tanning materials (polycondensed and polymerized compounds) were applied. TKO-type leathers were retanned using only aqueous acrylic polymer dispersions (*Retan 38* or *Syntan RS 3*). While in the case of NO-type leathers not only polymers, such as styrene copolymer and high molecular weight (above 100,000) acrylic polymer (*Derugan NG* and *Densotan A,* respectively), but also resins such as phenolic and dicyandiamide (*Ukatan NR* and *Ukatan AG*) were applied as retanning agents. In the case of NO-type leathers water repellents were introduced already at the neutralization and retanning stages: emulsifying amine modified fatty acids (*Limanol PEW*) and acrylic polymer (*Densotan A*) were used for the leathers NO-1 and NO-2, respectively.

After wet blue neutralization and retanning washing at elevated temperature ($T = 35\,°C - 40\,°C$) was performed. Then follows second cycle of chemical processing to increase leather fullness and impart water resistance properties. In the case of NO-type leathers practically the same resin and polymeric retanning agents as in previous stage were used (Table 2). For retanning with acrylic polymer to the TKO-type leathers additionally was added polycondensation product – resin *Syntan GP*.

For selective filling in the loosely structured parts of the leather, good grain tightness and fullness, high leveled dying, better buffing and finishing filling agents were used. In investigated cases were applied both types of fillers (syntans and natural tannins, i. e. vegetable).

The vegetable tans, such as hydrolysable tannin (chestnut in NO-type leathers) and condensed tannin (quebracho in TKO-2 leather) were applied. Lithuanian leather tanner added additionally the resin-like vegetable polymer, obtained by polyphenol copolymerization with an acrylic monomer (*Synektan R-982*) and protein filling agent (*Synektan F*).

The waterproofing of NO-type leathers were attempted to impart by using high molecular weight paraffines, silicone based additives and raw oil components (Table 2). The aqueous acrylic polymer solution (*Densotan A*), used in leather NO-2, has pronounced dispersing effect, therefore make waterproofing much easier, especially in the combination with *Densodrin* range products (BASF Group). The waterproofness of the TKO-1 leather was achieved by the repeated use of the mixture of emulsified synthetic oils *Synthol EW 321* with aqueous solution of acrylic acid and ester copolymer *Syncotan TL.*

In this chemical processing stage the coloring of leathers was performed as well (not discussed).

In the case of leathers NO-1, NO-2 and TKO-1 retanning, filling and fatliquoring proceeded in one solution at temperature 50 °C – 60 °C and pH = 3.7 – 3.8. For leather TKO-2 filling was carried out at temperature 30 °C, and after washing the fatliquoring with synthetic oils and anionic oiled paste was performed in distinct stage at temperature 60 °C and pH = 3.6 value.

After wet blue chemical processing obtained crust leather was finished using aqueous acrylic and polyurethane emulsions.

3.3. Testing

Scanning electron microscopy (SEM). SEM analysis of leather structure was performed using a microscope Quanta 200 FEG (FEI, Netherlands). All microscopic images were done on the same technical and technological conditions: the electron beam heating voltage – 20.00 kV, beam spot – 5.0, magnifications – 200× and 10000×, work distance – 6.0 mm, low vacuum –80 Pa, detector – LFD. For examination specimens about 1.2 mm thick crosscuts were made with a hand microtome.

Leather chemical analyses. Chromium content was determined according to the requirements of standard LST EN ISO 5398-1, which describes a method of the chromium in aqueous solution obtained from leather determination by iodometric titration.

The method of the matter soluble in dichloromethane (fatty substances) estimation specifies the standard LST EN ISO 4048. The extraction of fatty substances was carried out using Soxhlet apparatus.

The volatile matters, i. e. moisture, were determined using method described in LST EN ISO 4684. It is not possible to determine the exact moisture content of leather by this method. This is because at elevated temperatures other volatile substances escape and tannins and fats can be oxidized. Some absorbed water may be left in the leather after drying.

Determination of water resistance. Before testing all leathers were conditioned at standard atmosphere in accordance with the requirements of LST EN 12222 at a constant temperature $T = 23\,°C \pm 2\,°C$ and relative humidity $RH = 50\,\% \pm 5\,\%$ (23/50). Dynamic water resistance of leather using Bally Penetrometer, which specifies standards LST EN ISO 5403 and LST EN ISO 20344 was performed simulating conditions of wear. In this test a piece of leather was formed into the shape of trough and flexed whilst partially immersed in water. The water absorption as a percentage gain in mass of test piece due to the water uptake at the defined time was determined. Testing was carried out at standard atmosphere 23/50.

Determination of leather breathability. The method according to the requirements of standard LST EN ISO 14268 and LST EN ISO 20344 was used to test the water vapour permeability and absorption. The water vapour permeability was measured when test piece was fixed over the opening of a jar, which contains solid desiccant. This unit was placed in a strong current of air in a conditioned atmosphere (23/50). The air inside the container was constantly agitated by the desiccant, which was kept in movement by the rotation of the jar. The jar was weighted to determine the mass of the moisture that had passed through the test piece and had been absorbed by the desiccant.

In the case of water vapour absorption determination an impermeable material and the test piece was clamped over the opening of container, which holds water, for duration of the test (about 8 h). Water vapour coefficient was calculated using obtained values of permeability and absorption. Test piece was then weighted immediately and the water absorption determined by the mass difference before and after the test.

4. RESULTS AND DISCUSSIONS

Evaluation of the retanning and fatliquoring agents (see Table 2) shows that the waterproofness for TKO-type leathers mainly is achieved by filling the gaps in the fibre network with water-in-oil emulsion, while in NO-type leathers structure additionally is created using hydrophobic material net around the fibres without spaces filling. It is achieved by adding low surface energy silicone based products and hydrophobic esters.

The chemical materials defined in finished leathers are listed in Table 3. As it can be seen, in all leathers chromium content is similar and vary in the range of 4.48 % – 5.28 % (differs about 18 %). The same situation is observed in the case of volatile matter content (variation about 17 %). However, the matter soluble in dichloromethane (fatty substances) content in the leather depends on the fatliquoring technology. In the case of NO-type and TKO-1 leathers fatty substances content has close values (2.64 % – 3.82 %), while in the case of TKO-2 it is approximately twice large and reaches 6.71 % value. It may be supposed that such differences in dichloromethane soluble materials can be related to the TKO-2 fatliquoring in separate stage and influence of vegetable tannin quebracho (see Table 2).

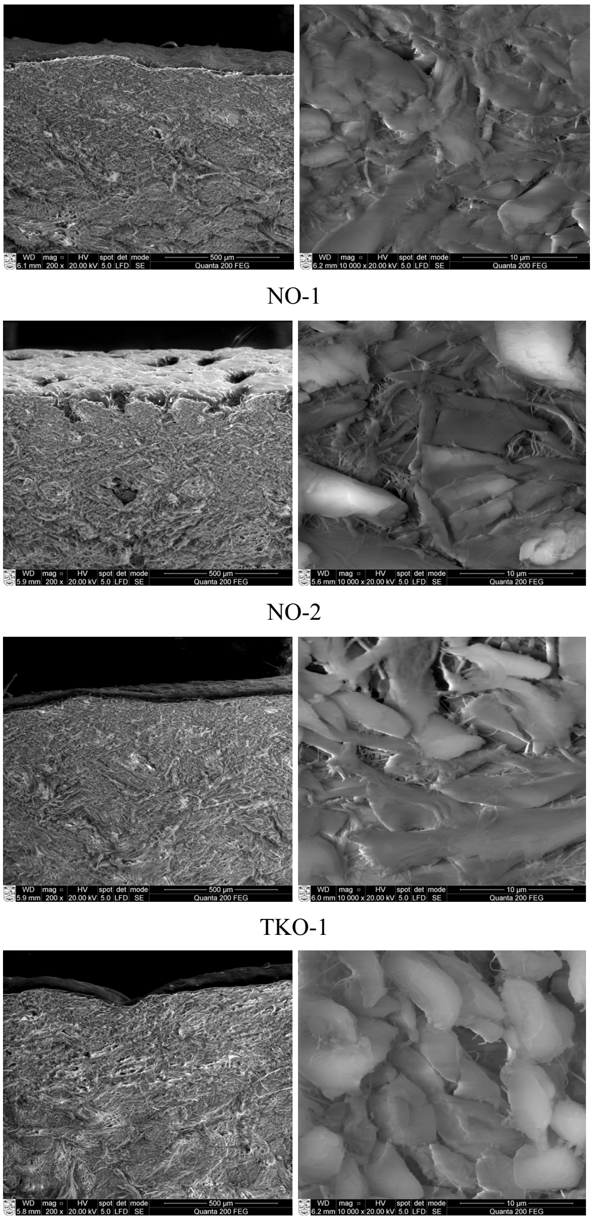
Table 3. Chemicals content in various leathers

Leather type	Content of chemical materials in leather, %:		
	chromic oxide	matter soluble in dichloromethane	volatile matter
NO-1	5.28	2.64	11.13
NO-2	4.56	3.34	11.24
TKO-1	5.09	3.82	12.39
TKO-2	4.48	6.71	13.00

Note: Cr(VI) content detected in of TKO-type leathers is in the range of (0.3–1.9) mg/kg (requirement Cr(VI) < 10 mg/kg)

The fibres weaving, fibre bundles splitting, separation and coalescence were investigated by SEM. The NO-type and TKO-type leathers cross-sections are shown in Fig. 3. Three-dimensional meshwork of modified collagen fibres can be seen. Collagen fibres bundles diameter is 2 μm – 5 μm and they are composed from many fibrils of variable thickness. From Fig. 3, a, it is evident the gradation in fibre size from coarse fibre bundles in the flesh and corium (central) regions, to the much finer fibrous structure found in the grain (outer surface) region. Due to the loss of protein during the preliminary stages of tanning, the regions between the top tightly-packed grain layer and next layer of intermediate fibre size loses cohesion and some delamination can occur. It is clearly seen in TKO-type leather cross-sections (Fig. 3, a).

The properties of leather depend on the individual fibres and their ability to move over each other. However, appearance of the fibres and their interweaving also reveals information about the processing through leather passes [1, 8]. The fibre bundles in NO-type leathers are packed more densely comparing to that of TKO-type leathers (Fig. 3, b). No visible differences in the NO-1 and NO-2 cross-section are seen. TKO-type leathers have large voids between fibre bundles; especially it is visible in TKO-2 leather. Besides, in some regions of TKO-1 leather the adhering of fibres to each other is detected, supposing due to the insufficient action of fatliquoring agents (Fig. 3, b). On the other hand, it may be related to the discrete leather quality, too [14, 16].



NO-1

NO-2

TKO-1

TKO-2

a b

Fig. 3. SEM images of various chrome tanned leathers cross-section at different magnification: a – 200×; b – 10 000×

Usually, it is required that military leathers would be water resistant by six hours at least [11]. It means that after six hours of dynamic testing that simulates conditions of wear, water absorption should be not higher than 25 % – 30 %. As it can be seen from Fig. 4, water absorption of leathers differs significantly and is dependent on leather quality, retanning and fatliquoring technologies. However, no water penetration was detected for all leathers during 7 h of testing.

It may be supposed that the cross-section of the NO-1 and NO-2 leathers is fully treated by retanning and fatliquoring agents during chemical processes. Therefore, even after 7 h under dynamic testing NO-1 and NO-2 leathers absorb only 5.7 % and 8.5 % of water, respectively. It can be noted that the replacement of water repellent silicone derivative and oil component (Schill+Seilacher) with aqueous acrylic polymer solution and silicone based component from BASF Group do not impart higher water resistance properties to the leather.

The leather TKO-2 obtained by using three-stage retanning and fatliquoring technology also shows high waterproofness after 7 h of testing (water uptake is 15 %). Another situation is observed with TKO-1 leather – already after 1 h testing the water absorption reaches 9 %. This value increases significantly during 4 h and 7 h of the testing (up to 22 % and 40 %, respectively). Thus, the waterproofness of TKO-1 leather is low, water repellant treatment is insufficient and this leather does not meet requirements for hydrophobic leather. Tough NO-type and TKO-2 leathers meet the requirements, but NO-1 and NO-2 leathers waterproofness is about 2 – 2.5 times higher. It may be dependent not only on the differences in leathers chemical processing, but mainly due to the low skin/hide quality used for TKO-type leathers production [9, 10].

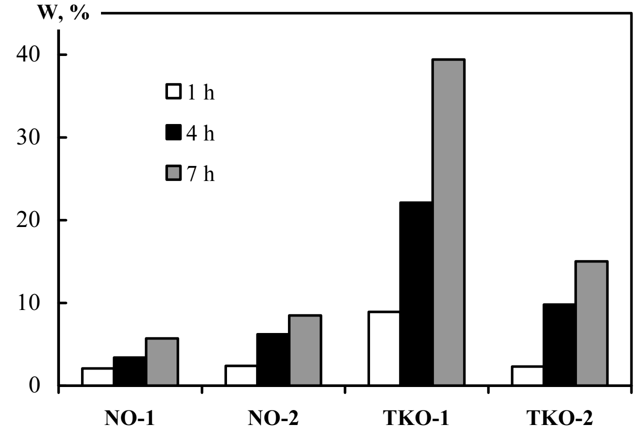
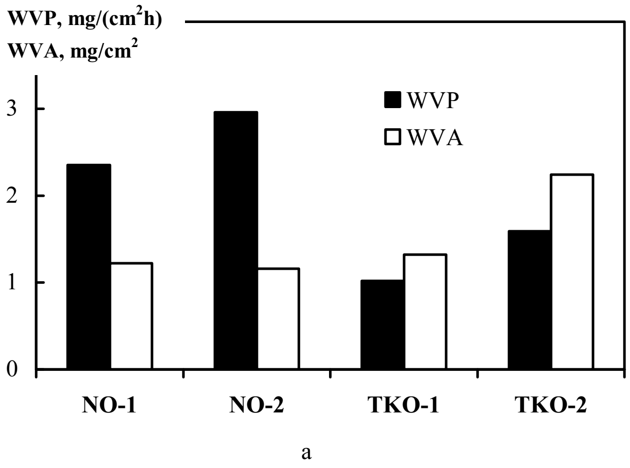


Fig. 4. Dependence of water absorption upon leather type at dynamic testing

While the penetration of liquid water should be prevented, water vapour should pass the leather as freely as possible, or at least be absorbed, to ensure good acclimatization inside of the footwear [4, 5]. Investigated leathers breathability is presented in Fig. 5. As can be seen, water vapour permeability (WVP) of leather TKO-1 is notably low, although the water absorption and penetration values are high (see Fig. 4). It may be related to the closed waterproofing that causes the sealing of pores with oil emulsions that impairs the water vapour permeability and absorption [2, 3]. On the other hand, the adhering of fibre bundles to each other due to the erratic penetration of chemicals can also reduce leather breathability. Meanwhile, WVP values for leathers NO-1 and NO-2 lies in the range of (2.5 – 3.0) mg/(cm^2·h) and satisfies requirements (WVP ≥ 0.8 mg/(cm^2 h)). The WVP value of TKO-2 is 1.5 – 1.9 times lower (1.6 mg/(cm^2·h)), but enough for perspiration evaporation.

From Fig. 5, a, it is evident that ability to absorb water vapour almost does not depend on the leather quality. WVA values are low and vary in the range of (1.16 – 2.24) mg/cm^2. It shows that after water repellent treatment interfacial tension between investigated leather fibres and water increases, and that significantly reduces or eliminates interaction with water.



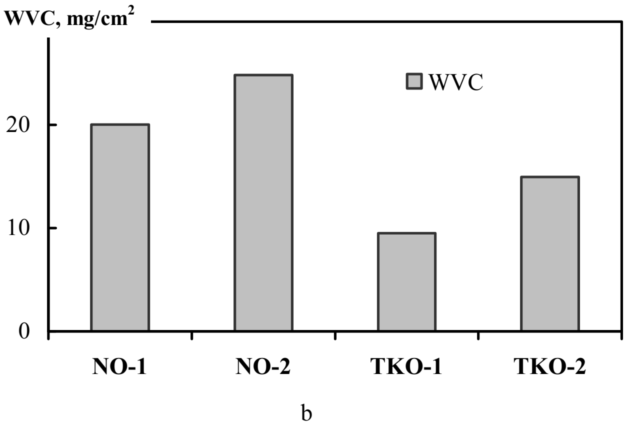


Fig. 5. Dependence of breathability upon leather type: WVP – water vapour permeability; WVA – water vapour absorption; WVC – water vapour coefficient

Water vapour coefficient depends upon water vapour penetration and absorption values ($WVC = 8 \cdot WVP + WVA$) and requires to be not less than 15 mg/cm^2. As can be expected after the evaluation of leathers water vapour penetration and absorption behaviour, TKO-1 leather shows insufficient WVC value – only 9.5 mg/cm^2 (Fig. 5, b). The coefficient values of NO-1 and NO-2 leathers are high enough and exceed requirement in 30 % and 60 %, respectively, while TKO-2 leather only scarcely satisfies required value.

Comparing NO-type leathers waterproofness and breathability behaviour it can be suspected that NO-2 leather has structure of less density, therefore show higher water vapour permeability, but lower water resistance than NO-1 leather.

5. CONCLUSIONS

The use of retanning compounds with free carboxylic groups, complex emulsifiers, and hydrophobic products, such as water insoluble fats and hydrophobic silicones allows obtaining leather with high water repellency properties and sufficient breathability. More effective are multifunctional fatliquoring agents, which are capable to surround the fibre with water repellent film and increase the surface tension with water. The water repellent treatment with chemical materials, which clog the interfibrillar spaces by water absorption and emulsion formation, ensures lower leather breathability.

Skin and hide quality influences on the finished leather structure and waterproofness. Properly selected chemical materials and their compositions with properly harmonized properties, also sufficient selected methods of such compositions application allow to produce leather with the desired properties even from the hide of low quality.

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