

FORMATION OF HYDROPHOBIZED LEATHER OF SPECIAL PURPOSE

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Abstract: *The influence of the chemical composition of the alkene-maleic composition on the water resistance, hygienic and physico-mechanical properties of the hydrophobized chrome tanned leather obtained from the leather of open cow is studied. It is established that hydrophobization of the leather semi-finished product with an alkene-maleic composition significantly increases the water resistance of the obtained leathers compared to unmodified ones, which results in an increase in the water-bathing time in dynamic conditions 35-47 times depending on the thickness and stability of the elastic-plastic properties of the leather during cyclic watering-drying. It is shown that with an increase in the thickness of hydrophobized leather from 1.8 to 2.4 mm, the water vapor permeability and air permeability decrease, respectively, by 1.2-1.6 and 1.5-1.7 times, at the same time, their hygroscopy increases by 10%. The complex physico-mechanical and hygienic properties of the leather, formed by the developed technology of hydrophobization of the chrome semi-finished product using alkene-maleic composition, meet the requirements of DSTU 2726-94 Leather for shoes and DSTU 3115-95 Leather for garments. As a result of the research, a technology for hydrophobization of semi-finished chrome tanned leather can be implemented in industrial production for the manufacture of water-repellent leather for special purposes.*

Keywords: *hydrophobization technology, semi-finished chrome tanning, alkene-maleic composition, special-purpose elastic leather, hygienic and elastic-plastic properties.*

1 INTRODUCTION

Natural leather, in comparison with synthetic materials, has a number of valuable advantages. This applies primarily hygienic properties. Such properties are due to the peculiarities of the porous structure of natural leather, the pore volume of which reaches 60%. At the same time, an important role belongs to such properties as pore size, their shape and size distribution. It should be noted that 45% of the pore volume can be considered macropores with sizes of 20-40 μm and 10% of micropores with sizes of 0.06-0.12 μm [1]. The nature of the porous structure of the leather and its chemical composition substantially depend on the effectiveness of the colloid-chemical processes of the technological cycle of processing raw leather.

For comfortable use of products made of natural leather in extreme conditions, it is necessary that the shoe upper material provides good vapor permeability, but is resistant to moisture in both static and dynamic conditions. Therefore, in after tanning processes, the chemical structure of natural leather is modified using different methods and compositions of different chemical composition.

During the formation of the leather of high water resistance, two types of composite materials are mainly used [1], taking into account the method of their use. At the same time, fatty and

hydroxycarboxylic acid esters and their derivatives, oxyethylated fatty acids, nitrogen-containing compounds, etc., are used for volumetric hydrophobization of the leather structure and others. It is known the use of polyorganosiloxanes with polyacrylates or fatty acid amides in the hydrophobization of a semi-finished product of chromium-free tanning [2]. The use of fluorine-containing silanes and polymers based on fluorocarboxylic acids [3] makes it possible to improve the performance properties of shoes made of leather split. Fluorosilane and fluoro siloxane have a persistent hydrophobic effect of leather tissue [4] with an increase in its strength. At the same time, wetting and moisture holding capacity are reduced by three times, its watering increases from 5 to 170 minutes and the elasticity of the hair without reducing hygienic properties.

The use of the maleic acid ester copolymer and α -hydroxypropyldimethylsiloxane at a ratio of 2:1, acrylic acid and 1-octadecane by the authors of works [5, 6] made it possible to significantly increase the resistance of leather and elasticity of the leather. When used to hydrophobize a semi-finished product of polyethylhydroxyloxane acrylate polymers [7], tanning and film-forming effects are observed. In work [8], the authors used to hydrophobize compositions based on polyvinyl ethylene dihydroxychlorosilane, which was applied

by spraying. Hydrophobic leather surface with a wetting angle of 110° is achieved in this case. This effect is reduced to 94° after 300 cycles of erasure on the device "ACL-1". When using the composition of organosilicon compounds modified with fluorotoluene, a significant reduction in water wetting and water penetration of the leather in dynamic conditions is achieved [9]. This increases the heat-shielding properties of the material. An increase in the hygienic properties of hydrophobized leathers has been established [10] due to the use of a composition that includes the reaction products of an amino alcohol with fatty acids of vegetable oils of the C₁₂₋₂₂ fraction and boric acid at their molar ratio of 2:1:1 in mineral oil.

To determine the effect of retanning agents of synthetic polymers and plant extracts in the hydrophobization of white leather, fluoride-woven compound was used [11]. At the same time, the hydrophobic effect is more reduced due to the use of acrylic polymer and Inditan RS dispersing agent in addition. The effect of fat emulsions based on rapeseed oil and fish oil triglycerides on the sorption-desorption process and the mechanism of water diffusion into the structure of the processed semi-finished product was investigated by the authors of [12]. The dependence of the diffusion of water into the semi-finished product on the humidity of the medium is established. The use of non-equilibrium low-temperature plasma can be attributed to innovative methods of hydrophobization of semi-finished leather-fur [13, 14]. When using an argon/propane-butane gas mixture in the 70/30 ratio, as a result of the decomposition of hydrocarbons, carbon is formed, which is adsorbed on the surface of leather elements and ensures its long-lasting hydrophobization.

For improve the water resistance of the leather in dynamic conditions, Lubritan XS product of Lanxess (Leverkusen) and Rohm and Haas (Philadelphia), a special silicone polymer can be used by [15]. These two products can be used to obtain waterproof leather with individual properties of the desired quality of [15], however, the publication does not indicate the duration of the hydrophobic effect. Thus, despite the wide range of water-repellent compositions and various ways of using them, the results of determining the effect of waterproofing under dynamic conditions are practically absent. In this regard, it is difficult to objectively evaluate how the water-repellent action of the corresponding composition and methods of its use for the production technologies of elastic hydrophobic leathers.

The aim of research is studying the influence of the conditions of hydrophobization-retanning of a leather semi-finished chrome tanning using alkene-maleic compositions on the complex

of structural-mechanical and operational properties of the leather. The following tasks were solved:

- determination of the effect of the composition of alkene-maleic-containing composition on the physico-chemical properties of the leather;
- study the effect of the thickness of the semi-finished product on the sorption-diffusion properties of the resulting leather;
- studies of the restorability of the porous structure of the hydrophobized leather and the physico-mechanical properties of the material obtained by the developed technology, while modeling the mode of its operation;
- establishment of hydrophobization parameters of leather semi-finished chrome tanning of various thickness.

2 MATERIALS AND METHODS

Samples of semi-finished chrome tanning products from cattle raw materials - medium open cow, manufactured according to the technology of Chinbar PJSC (Ukraine, Kyiv) and plane for 1.2-2.4 mm thickness were subject to research. Samples with a size of 180x300 mm were cut out from the area of a plane semi-finished blanked by the method of symmetrical strips. Prototypes after washing and neutralizing the subunit with the use of 7% vegetable extract of quebracho based on the weight of the semi-finished product. For the control samples, a mixture of acrylic polymer Relanal RCN-40 from the company Cromogenia-Units, S.A. (Spain), synthetic tanning material Relugan D from BASF (Germany) and Quebracho extract (China), wt.% respectively 3, 5 and 6. The hydrophobization of the chrome semi-finished product was carried out in a laboratory drum with a volume of 10 dm³ while rotating at a speed of 12-14 min⁻¹. Prefabricated prototypes with thicknesses of 1.2; 1.8 and 2.4 mm (respectively, D-1.2, D-1.8, D-2.4) were treated with an alkene-maleic composition (AMC) containing an alkene maleate polymer (AMP) [16], oleic acid (OA) and cod liver oil (CLO) followed by fixing the ingredients of the composition of potassium alum (Table 1).

Control semi-finished unmodified samples (CU-1.8) after neutralization were treated with fish oil composition/sulfite fish oil composition/synthetic fat at a ratio of 1/4/5, and modified (CM-1.8) – only AMP. The resulting samples of the leather semi-finished product, after aging for 48 hours, were pressed, dried, moistened, kneaded, dried, stretched and conditioned for 24 hours.

The study of the chemical composition and physico-mechanical properties of the leather samples was carried out according to the methods of [17]. Moisture content in the leather was determined by gravimetric method at 100-105°C. The total ash was determined thermogravimetrically after oxidizing the sample (7.5 g) in porcelain crucibles at 600°C.

Table 1 Hydrophobization parameters of chrome tanned semi-finished product

Process	Reagent	Yield [%]	Duration [min]	Temperature [°C]
Washing	Water	200	10-15	32-36
Drain				
Neutralization	Water	120	60	32-36
	Sodium formate	1		
	Sodium bicarbonate	1		
Washing	Water	200	10-15	40-42
Drain				
Retanning-filling	Water	70-80	60-80	40-42
	Queberacho natural extract (solution)	6-7		
	Sodium sulfite	0.6-0.7		
Hydrophobization-fatting	Water	100	40-60	55-60
	Alkene-maleic polymer	4.0-4.5		
	Oleic acid	1.2-1.3		
	Cod liver oil	6.0-7.0		
Fixation	Aluminium potassium sulfate	0.4-0.5	20-30	55-60
	Sodium formate	0.3-0.4		
Washing	Water	200	10-15	22-25
Drain				

Note: The process duration, depending on the thickness of the planed semi-finished product

The content of substances extracted with organic solvents (unbound fat) was determined using a Zaichenko extraction apparatus. A crushed sample (5 g) within a paper shell was put into the extractor and solvent extraction with tetrachloromethane was carried out for 1.5 h. After solvent evaporation under vacuum, the fatty substances were dried in an oven at 128-130°C for 1 h. After cooling the flask in the desiccator, the flask with unbound fat was weighed and the mass fraction of unbound fat was calculated.

Bound fatty substances were determined after removal from a sample of UFS (unbound fatty substances) by their hydrolytic destruction with an alcoholic solution of sodium hydroxide, followed by extraction of fatty acids with diethyl ether. The protein content was estimated based on nitrogen content determined by the Kjeldahl method. Chromium content was determined by iodometric titration and expressed as the mass fraction of chromium (III) oxide.

Porosity of leather was determined by the ratio of pore volume to the sample apparent volume [%]. Volumetric yield was determined by the ratio of the volume of an air-dry leather sample to the volume calculated as a product of the sample mass and sample apparent density.

Vapor permeability was determined by desiccator method using sulfuric acid. The air permeability of the leather was determined by the volume of air that penetrated in 1 h through 1 cm² of the leather sample at a pressure difference on both sides of the sample of 1 kPa.

Hygroscopicity was determined by the increase in the mass of leather samples kept in a desiccator over water for 16 h. The mass of the air-dried samples were used for comparison. Moisture release was determined by the amount of moisture lost by the leather sample (hygroscopically

moistened) during air drying for 8 h under normal conditions.

In determining the water wetting of leather in dynamic conditions (WDC), minutes, the used equipment "DWD-2" (RF) and "IG/IUP 10" by Giuliani (Italy) at a deformation rate of 24, 70, 120 and 52 min⁻¹, respectively. The properties of leathers with spherical deformation were evaluated on a DOTL device (Ukraine) using a punch with a hemisphere radius of 5 mm. The physico-mechanical properties of the output leathers, after contacting them with water at a temperature of 20-22°C for 24 hours, their drying in a free state and conditioning of the same duration were evaluated on a PT-250M (RF) machine at a deformation rate of 90 mm/min. At the same time, the following are determined: tensile strength [MPa]; elongation under load 9.81 MPa L_{9.8} [%], and other indicators. Determination of stiffness [cN], and elasticity [%], indicators (respectively, S and E) was carried out on a DSE-12M device (RF) with cyclic drenching-drying of samples of hides of size 20-160 mm. The relative error in determining the sorption-diffusion parameters was 3-4%, the physico-mechanical characteristics were 5-7%.

3 RESULTS AND DISCUSSION

In this paper, a complex of studies of the physico-chemical properties of leather obtained using the results of a study of the effect of AMC composition on the physico-chemical properties of leather 1.8 mm thick are given in Table 2.

The data show that with an increase in the AMP content in the composition in the presence of oleic acid, the duration of watering under dynamic conditions at a deformation rate of 24 min⁻¹ reaches an extreme value. The value of this indicator is stabilized for the composition of option 2 and compared with the control option is more than 32%.

Table 2 Physical and chemical properties of the leather, modified by alkene-maleic composition

Composition content	Ingredients [%]*			Indicators			
	AMP	OA	CLO	WDC-24	σ	L _{9,8}	S
1	3.75	0.90	5.50	187	22.0	29.0	26.0
2	4.25	1.20	4.50	317	23.5	30.0	25.8
3	4.75	1.40	3.50	290	22.8	25.0	29.5
CM-1.8	4.50	–	–	240	20.5	26.0	35.0

Note: *semi-finished product mass

In a similar way, as well as the water treatment of the leather, with changing composition of the composition, its physical and mechanical properties change. At the same time, the elasticity of the samples reaches a maximum value, and the minimum hardness for leathers obtained by modifying a semi-finished product with compositions of the same variants. Introduction to the modifying composition of oleic acid makes it necessary to increase the degree of CLO dispersion.

So, when modifying a chrome semi-finished product with an alkene-maleic mixture, the adequacy of the ingredients is, wt. %: AMP:OA:CLO as 4.25:1.2:4.5 achieved the hydrophobic effect of maximum magnitude. It is possible to obtain elastic leather with minimum stiffness and maximum elongation under a load of 9.81 MPa.

During the operation of leather products, especially hydrophobized, its thickness and layer-by-layer structure are essential, from which the effectiveness of the process of hydrophobization and, accordingly, operational properties of such products. The response of the structure of the modified leather, to a large extent, depends on the conditions of its deformation, the effectiveness of the hydrophobization, the interaction with the fibrillar structure of the leather semi-finished product of the modifier ingredients and their distribution in its volume.

According to the obtained data (Table 3), an increase in leather thickness is accompanied by an increase in the duration of its watering.

Table 3 Water wetting of leather with a modified alkene-maleic-content composition under dynamic conditions

Leather	Water wetting [min] at speed of specimen deformation [min ⁻¹]			
	24	52	70	120
D-1.8	315	276	243	190
D-2.4	337	298	265	207
CM-1.8	240	226	200	158
CU-1.8	9	7	5.5	4

At the same time, the duration of water treatment of modified leather is significantly longer compared to control-modified and unmodified leather, especially compared to unchanged, respectively, by 1.2-1.3 and 35-47 times, depending on the rate of deformation of the samples.

That is, the effectiveness of the hydrophobization of the leather structure is manifested in the degree of reduction of watering with an increase in the rate of deformation of its samples. At the same time, the increase in the deformation rate is five times, which is accompanied by a decrease in the length of the water wetting by 1.6-1.7 times.

Additional information on the interaction of hydrophobized leather with water can be obtained by examining wetting in static conditions. The kinetics of wetting of the modified leather of prototypes D-1.8 (Figure 1) indicates a significant increase in mass only after five hours of contact with water, and after 24 hours their mass increases to 38%. Non-hydrophobized samples after 1 h increase the mass to 75%, reaching 160% in a day. Compared to the control-modified samples, the prototype has a lower degree of wetting at 5 and 24 hours by 33 and 17%.

Thus, the use of an alkene maleate composition in the presence of oleic acid makes it possible to significantly reduce the hydrophilicity of the leather structure, especially when compared with the unmodified version. The research results of the effect of the thickness of the hydrophobized leather on the complex of its sorption-diffusion characteristics are given in Table 4.

Table 4 Sorption-diffusion properties of the developed leather

Indicator	Leather		
	D-1.8	D-2.4	CU-1.8
Porosity [%]	55.0	57.0	51.0
Volume yield [%]	243.0	256.0	217.0
Vapor permeability [mg/cm ² ·h]			
from the side - flesh	11.2	7.1	14.0
- facial	2.3	1.9	3.9
Air permeability [cm ³ /cm ² ·h]			
from the side - flesh	790.0	540.0	370.0
- facial	630.0	370.0	290.0
Hygroscoy [%]	12.1	13.3	11.7
Water-yielding capacity [%]	5.7	5.1	2.6

The increase in the porosity of the hydrophobized leather in comparison with the control samples may indicate the formation of a more developed fibrillar structure. This leads to an increase in the volume output of the leather by 12-18% and the preservation of its finely dispersed fibrous structure after carrying out drying and moisturizing processes and operations.

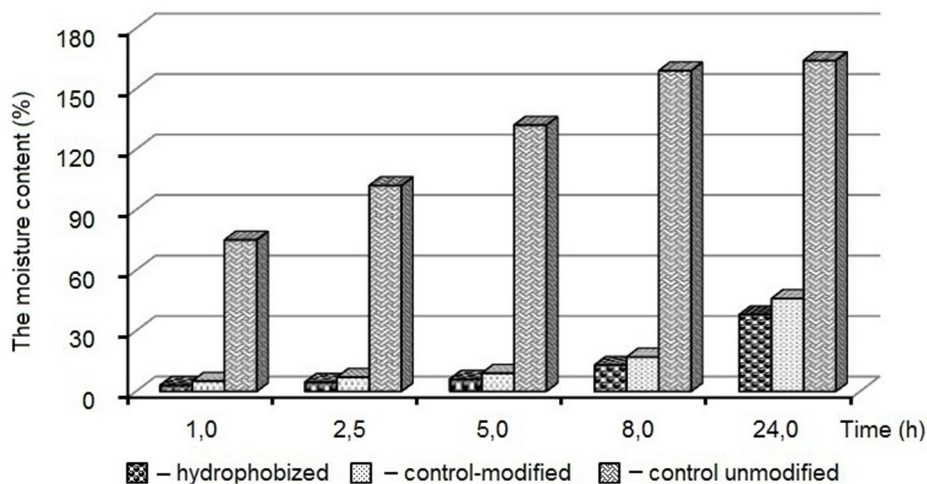


Figure 1 Wetting kinetics of leather

A significant increase in air permeability of the research leather D-1.8 and D-2.4 compared to unchanged by 2.1-2.2 and 1.3-1.5 times, respectively, may indicate the presence of a significant number of through pores. The higher relative air permeability of the leathers from the flesh side compared with the control sample indicates an increased porosity of the flesh layer of hydrophobized leather.

The effect of vapor permeability of hydrophobized leather compared to unchanged may be due to the complex transport mechanism of water vapor based on sequential processes of their sorption and desorption. This may indicate the presence of a significant number of pores of smaller sizes in the leather D-1.8, which facilitate the process of condensation of water vapor, on the one hand, and complicate their transportation through the thickness of the leather. Features of the porous structure of experimental samples explain the nature of the change in hygroscopy and moisture return of hydrophobized leather, which depend on the thickness and composition of hydrophobic-fat composition. Thus, the moisture return of the leather, the fattened, and the alkene-maleic composition with the addition of oleic acid is 2.0-2.2 times higher than that of the non-hydrophobized leather.

So, the conducted studies indicate a significant influence of the hydrophobization process both on the nature of the porous structure of the leather – the ratio of micro- and macropores, and hydrophilicity, due to the interaction of the ingredients of alkene - maleic - content compositions with the surface of the fibrillar collagen structure of the chrome semi-finished product. The inadequacy of changes in the indicators of hydrophobized leather compared with only their collagen structure, which in terms of air permeability, moisture return and volume output significantly exceeds the non-hydrophobized, is established.

Analyzing the effect of leather thickness on its chemical composition (Table 5), it can be noted that modified leather is characterized by a high content of bound fatty substances. It should be noted that the amount of chemically related fatty substances in the leather structure is greater in the case of a smaller thickness.

Table 5 The chemical composition of hydrophobized leather

Mass content [%]	Leather		
	D-1.8	D-2.4	CU-1.8
moisture	11.26	11.98	12.32
chromium oxide	4.38	4.32	4.43
ash	6.53	6.36	6.18
substances extracted with organic solvents (SEOS)	9.12	8.27	8.34
bound fatty substances	4.18	3.98	1.32
crural substance	61.57	62.69	65.38

Note: Mass content of leather ingredients are given in terms of absolutely dry substance

Due to the layer-by-layer study of the hydrophobized leather D-2.4 (Figure 2), it is established that the content of both bound and unbound fatty substances in large quantities is contained in the facial layer.

This distribution of fatty substances is due to the structural features of the facial layer after hair removal and destruction of hair follicles located in the papillary layer. The content of bound fatty substances in the papillary and flesh layers is 2.2 times and 1.6 times higher than the middle layer. The obtained result may be due to the effective interaction of the ingredients of the developed composition with the structure of the leather semi-finished product. At the same time, a decrease in the chromium (III) oxide content in the middle layer of the leather is observed as compared with the outer layers by 30-40%.

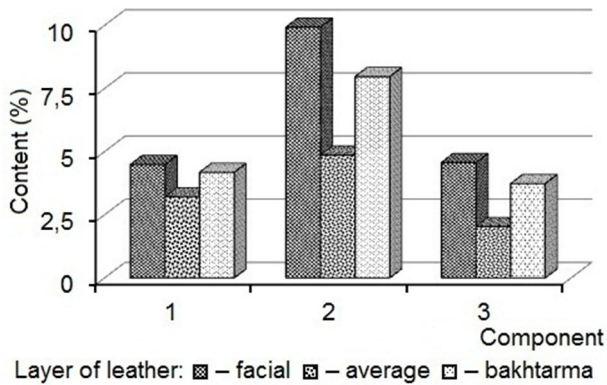


Figure 2 Layered content in leather material [wt.%]: 1 - chromium oxide, 2 - SEOS, 3 - bound fatty substances

So, the most uniform layer-by-layer distribution in hydrophobized leather is observed for chromium (III) oxide, and the distribution of bound fatty substances is the least uniform, with the highest content in the facial layer. At the same time, the absolute values of the amount of bound fatty substances in hydrophobized leather are three times more than non-hydrophobized.

The complex of physico-chemical characteristics of leather, mainly determines their operational properties. The results of the study of physico-mechanical parameters of hydrophobized leather of various thicknesses before and after their contact with water are given in Table 6.

From the obtained data it is clear that the samples of hydrophobized leather after contact with water

show a slight decrease in strength with almost the same values of indicators of the appearance of cracks of the face layer compared with the values of the initial samples. At the same time, the elastic deformation of the hydrophobized specimens D-1.8 and D-2.4 grows over the output, respectively, by 15 and 18% with an increase in the residual elongation by 39 and 30%. It should be noted that samples of non-hydrophobic leather are characterized by a decrease in strength by 13%, an increase in deformation indicators by 17-21% and an elastic elongation only by 7.0% with a significant increase (81%) of the residual elongation.

So, leather hydrophobized by AMC in the wet state have increased elastic-plastic properties compared to unmodified leathers.

During cyclical watering-drying, the strength characteristics of both hydrophobized and unmodified leathers change in a similar way during spherical deformation after their contact with water (Table 7).

With complex deformation of hydrophobized specimens in the wet state, the strength values of the leather, the face layer and elongation change in the same way. At the same time, the meridional elongation increases by 13-15%, and after drying, both their strength and elongation practically correspond to the values of the physico-mechanical parameters for the output leathers. The strength of samples of unmodified leather increases slightly with decreasing meridional elongation.

Table 6 Physico-mechanical properties of the leather during uniaxial deformation

Indicator	Leather			
	D-1.8	D-2.4	CU-1.8	
Ultimate tensile strength [MPa]	22.0/21.3	25.0/24.0	23.2/ 20.5	
The appearance of cracks of the facial layer [MPa]	22.0/21.3	25.0/24.0	21.0/20.5	
Elongation [%]	under load 9.81 MPa			
	rupture	36.0/39.0	34.0/37.8	37.0/42.0
	residual	46.0/54.0	43.0/52.0	53.0/63.0
	elastic	8.7/12.1	9.9/12.9	9.2/22.1
		37.3/42.9	33.1/39.1	42.8/40.9

Note: Numerator and denominator correspond to dry and wet leather

Table 7 Physico-mechanical properties of the leather during spherical deformation

Indicator	Leather					
	initial ¹			after drying		
	D-1.8	D-2.4	CU-1.8	D-1.8	D-2.4	CU-1.8
Strength of leather [N]	580 565	730 705	540 475	575	710	570
Strength of the facial layer of leather [N]	580 565	720 705	430 380	575	710	420
Elongation [%] with	appearance of cracked facial layer			60.0	53.0	30.0
	leather breakthrough			60.0	53.0	41.0

Note: ¹Numerator and denominator correspond to dry and wet leather

Table 8 The stiffness and elasticity of the leather after cyclic watering-drying

Leather	initial ¹		after drying	
	S [cN]	E [%]	S [cN]	E [%]
D-2.4	36/24	56/31	38	59
D-1.8	27/21	53/29	29	57
D-1.2	21/16	51/26	20	55
CU-1.8	29/15	58/20	36	64

Note: ¹Numerator and denominator correspond to dry and wet leather

Accordingly, after contact with water, the indicators of stiffness and elasticity of the samples change with their large absolute values in the second case (Table 8).

During the restoration of the moisture content in the leather during drying, the rigidity and elasticity of the hydrophobized specimens remain almost unchanged, and the unmodified specimens show an increase in rigidity and elasticity, respectively, by 24 and 10%. It should be noted that with an increase in the thickness of hydrophobic leather twice the stiffness index increases 1.7 times.

Thus, according to the changes in the elastic-plastic properties in the process of cyclic watering-drying of hydrophobized leathers, their structure is effectively restored.

Based on the carried out complex of sorption-diffusion and physicochemical studies of the properties of hydrophobized leather using AMC of different chemical composition, a technology has been developed for the formation of the hydrophobic properties of elastic leather of special purpose (Table 1).

According to the developed technology, the chrome semi-finished product obtained by Chinbar PJSC technology after pressing and planing to the required thickness was to be neutralized to a pH of the spent solution of 5.8-6.0. The following retanning-filling is performed using plant extract, in particular quebracho, when adjusting its solution with sodium sulphite to an initial pH of 5.8-6.0. Hydrophobization-fattening semi-finished product is carried out on the spent solution after raising its temperature to the required by adding the appropriate volume of water with a temperature of 80-85°C. Then the calculated amount of required materials is added to the drum. At the end of the process, the pH of the working solution is reduced to 4.0-4.2 aluminum potassium sulfate for fixing the reagents in the semi-finished product. In this case, oleic acid aluminate is formed, which enhances the effect of hydrophobization of the structure of the semi-finished product. The following drying and moisturizing processes and operations, namely: extracting, dilution, drying, moisturizing, stretching, pressing the obtained leathers are performed according to the technology of Chinbar PJSC.

Consequently, taking into account the results of the study of the properties of the obtained leather

semi-finished product at the retanning-hydrophobization stage, a technology for the formation of hydrophobic leathers has been developed, which can be recommended for introduction into the technological cycle of industrial production of elastic leather for special purposes.

4 CONCLUSIONS

The hydrophobization process of semi-finished chrome tanned leather of various thicknesses using alkene-maleic composition for the manufacture of elastic leather for special purposes was studied.

It is established that the hydrophobization of the leather semi-finished product with the alkene-maleic composition significantly increases the water resistance of the obtained leathers compared to unmodified ones, which is reflected in an increase in the water-watering time in dynamic conditions 35-47 times depending on the thickness and stability of the elastic-plastic properties of the leather during cyclic watering-drying.

It is shown that with an increase in the thickness of hydrophobized leather from 1.8 to 2.4 mm, vapor and air permeability decreases by 1.2-1.6 and 1.5-1.7 times, respectively, while their hygroscopy increases by 10%.

The nature of the changes in the physico-mechanical properties during watering-drying of the leather semi-finished product indicates the plasticization effect of water on the collagen structure of the chromium semi-finished product, which causes the formation of additional inter-fibrillar bonds.

According to the complex of physico-mechanical and hygienic properties of the leather, formed according to the developed technology of hydrophobization of the chrome semi-finished product using alkene-maleic compositions, they meet the requirements of DSTU 2726-94 Leather for Upper Shoes and DSTU 3115-95 Leather for garments.

As a result of the research, a technology for hydrophobization of semi-finished chrome tanned leather can be implemented in industrial production for the manufacture of hydrophobized leather for special purposes.

5 REFERENCES

1. Nikolayenko G.R.: Modern methods of hydrophobization of natural materials, Bulletin of Kazan Technological University 8, 2014, pp. 79-83, <https://cyberleninka.ru/article/n/sovremennye-metody-gidrofobizatsii-naturalnyh-materialov-legkoy-promyshlennosti/viewer>
2. Meyndt R., Germann H.P.: The hydrophobing of chrome-free leather, World Leather 8(49-50), 2007, pp. 52-54
3. Nizamova Z.K., Kalinin M.V., Evsyukova N.V., et al.: Evaluation of the effectiveness of drugs for surface hydrophobization split, Leather and Footwear Industry 2, 2012, pp. 18-19
4. Evsyukova N.V., Vorobyova I.V., Polukhina L.M., et al.: Hydrophobization of leather-fursemi-finished product with fluorine-containing functional silanes and siloxanes, Design and Technology 11, 2009, pp. 68-72
5. Dahmen K., Mertens R.: Use of siloxane copolymers for treating leather and pelts, Leather Sci. Abstr. 1, 1995, pp. 9-10
6. Kovacevic V., Babic R.: Achieving resistance to water for special purpose leather, Koza i obuca (Leather and Shoes) 42(11-12), 1993, pp. 127-128
7. Dzhurav A.M., Kadirov T.Z., Toshev A. Yu.: The effect of hydrophobization on the performance properties of leather for upper shoes, Leather and Fur in the 21st Century: Technology, Quality, Ecology, Education 2015, pp. 48-54, https://esstu.ru/library/free/Konf/Kozha_2015/7_%D0%94%D0%B6%D1%83%D1%80%D0%B0%D0%B5%D0%B2_%D0%9A%D0%B0%D0%B4%D0%B8%D1%80%D0%BE%D0%B2_%D0%A2%D0%BE%D1%88%D0%B5%D0%B2.pdf
8. Akhmedov V.N., Dzhuraev A.M., Toshev A.Yu., et al.: Polyethylhydroxyloxane acrylate polymers to enhance the hydrophobization effect, Chemical Technology 5, 2007, pp. 145-146
9. Ermolenko N.V., Guryanova T.I., Platonov V.Ye., Puchkina G.A., et al.: On the effect of a fluorine-containing compound on the hydrophobic properties of the leather, Leather and Footwear Industry 3, 2003, pp. 30-31
10. Pat. 2404260 Russia, IPC C14C 13/00, C14C9/00, C14C9/02, C14C3/14, C14C3/28. Method for the production of hydrophobic leathers, Studenikin S.I., Yakovlev K.P., Bogomolov V.G., et al.; Applicant and patent holder Ministry of industry and trade of the Russian Federation; stated. November 6, 2009; published 11/20/2010, <http://www.freepatent.ru/patents/2404260>
11. Silva V.F.M., Moncada M., Crispim A., Cruz T., Crispim F.: Studies on waterproofing wet-white leather, Leather and Footwear Journal 18(2), 2018, pp. 149-152, <https://doi.org/10.24264/lfj.18.2.10>
12. Manich A.M., Barenys J., Martínez L., Martí M., Carilla J., Marsal A.: Effect of fatliquoring and finishing on moisture absorption-desorption of leather, Vlakna a textil (Fibres and Textiles) 23(3), 2016, pp. 117-125
13. Nikolayenko G.R., Shestov A.V., Kulentsov G.N.: Hydrophobization of special-purpose leathers by treatment with non-equilibrium low-temperature plasma, Technologies and Design 3(8), 2013, pp. 1-8, (Electronic resource), http://nbuv.gov.ua/UJRN/td_2013_3_11
14. Kulentsov G.N., Stepin S.N., Nikolaenko G.R., Semenova E.N., Shestov A.V., Mingaliev R.R.: "Cold plasma" and nanomaterials as a promising method for improving the hygienic properties of special-purpose leathers for oil and gas workers, Bulletin of Kazan Technological University 5, 2013, pp. 59-62, <https://cyberleninka.ru/article/n/holodnaya-plazma-i-nanomaterialy-kak-perspektivnyy-metod-povysheniya-gigienicheskikh-svoystv-kozh-spetsialnogo-naznacheniya-dlya/viewer>
15. An innovative solution for waterproofing, Leather international, 12 April, 2007, (Electronic resource), <http://www.leathermag.com/features/featurean-innovative-solution-for-waterproofing-leather/>
16. Pat. (Utility model patent) 38472 Ukraine, IPC C14C 9/00. Composition for hydrophobization of pile leather, fur velor, fur sheepskin and articles thereof, Danilkovich A.G., Khlebnikova N.B., Mokrousova O.R., Petko K.I.; Applicant and patent holder Kyiv National University of Technologies and Design, № u200810214; stated. August 08, 2008; published 01/12/2009; bullet №1, <http://uapatents.com/3-38472-kompoziciya-dlya-gidrofobizaci-vorovo-shkiri-khutrovogo-velyuru-shubno-ovchini-i-virobiv-z-nikh.html>
17. Danilkovich A.G., Chursin V.I.: Analytical control in the production of leather and fur: A laboratory workshop: Textbook, Allowance, Moscow: INFRA-M, 2016, 176 p., <https://doi.org/10.12737/17702>