INFLUENCE OF SOLAR RADIATION INSOLATION PRECIPITATION ON HYDROPHOBIZED LEATHER FOR SHOE UPPERS

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Received: 27.03.2021 Accepted: 18.08.2021 https://doi.org/10.24264/lfj.21.3.3

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ABSTRACT. The influence of solar radiation and precipitation on leather samples for the upper part of footwear, treated with water-repellent compounds, was determined and the process of their destruction in natural atmospheric conditions was determined. The study of the effect of solar radiation on natural skin has not been sufficiently studied. In connection with the above, the test was carried out on experimental hydrophobized and initial (control) leather samples in an open area to determine the insolation of solar radiation and precipitation on the skin for the upper shoes. During the tests, a systematic examination of the exposed samples was carried out for 1-6 months, sampling for physico-mechanical and other tests was recorded by meteorological conditions. After that, the samples were subjected to organoleptic evaluation, physical-mechanical and chemical-analytical analyses, as well as structural studies. It was visually determined that, depending on the variant of hydrophobization used, fibrillar collagen formations change in different ways. After atmospheric insolation acts on the control sample, its fibrillar structure changes sharply, numerous micro cracks appear, located mainly perpendicular to the fiber axis, and clearly defined dark zones are found between the fibrils. Fibril outlines become indistinct, numerous torn ends are observed. However, such changes are not observed for hydrophobized samples. Significant changes in physical and mechanical properties are observed in the first and fourth months of natural aging. In the hydrophobized sample, the rate of change in hydrothermal destruction and the appearance of cracks in the face layer subjected to aging in an open area, is always lower compared to the control sample.

KEY WORDS: hydrothermal destruction, hydrophobization, insolation of solar radiation, destruction, fibrillar structure

INFLUENȚA RADIAȚIEI SOLARE ȘI PRECIPITAȚIILOR ASUPRA PIELII HIDROFOBIZATE PENTRU FEȚE DE ÎNCĂLȚĂMINTE

REZUMAT. S-a determinat influența radiației solare și a precipitațiilor asupra probelor de piele pentru fețe de încălțăminte, tratate cu compuși hidrofugi, precum și procesul de distrugere a acestora în condiții atmosferice naturale. Efectul radiației solare asupra pielii naturale nu a fost suficient studiat până acum. În legătură cu cele de mai sus, prezentul studiu a fost efectuat pe probe experimentale de piele hidrofobizată și în stare inițială (martor) într-o zonă deschisă pentru a determina influența radiației solare și a precipitațiilor asupra pielii pentru fețe de încălțăminte. În timpul testelor, s-a efectuat o examinare sistematică a probelor expuse timp de 1-6 luni, s-au prelevat probe pentru teste fizico-mecanice și alte teste în funcție de condițiile meteorologice. După aceea, probele au fost supuse evaluării organoleptice, analizelor fizico-mecanice și chimice, precum și analizelor structurale. S-a determinat vizual că, în funcție de varianta de hidrofobizare utilizată, formațiunile de colagen fibrilar se schimbă în moduri diferite. După acțiunea radiației solare și a atmosferei asupra probei martor, structura fibrilară a acesteia se schimbă brusc, apar numeroase microfisuri, situate în principal perpendicular pe axa fibrelor și se constată zone întunecate clar definite între fibrile. Contururile fibrilelor devin indistincte, se observă numeroase capete rupte. Cu toate acestea, astfel de modificări nu se observă în cazul probelor hidrofobizate. Modificări semnificative ale proprietăților fizice și mecanice sunt observate în prima și a patra lună de îmbătrânire naturală. În cazul probei hidrofobizate, rata de modificare în ceea ce privește deteriorarea hidrotermică și apariția fisurilor în stratul de suprafață al probei supuse îmbătrânirii într-o zonă deschisă, este întotdeauna mai mică comparativ cu proba martor.

CUVINTE CHEIE: deteriorarea hidrotermică, hidrofobizare, radiație solară, distrugere, structură fibrilară

L’INFLUENCE DU RAYONNEMENT SOLAIRE ET DES PRÉCIPITATIONS SUR LE CUIR HYDROPHOBE POUR LES TIGES CHAUSSURE

RÉSUMÉ. L’influence du rayonnement solaire et des précipitations sur les échantillons de cuir pour les tiges de chaussures, traitées avec des composés hydrofuges, ainsi que le processus de leur destruction dans des conditions atmosphériques naturelles ont été déterminés. L’effet du rayonnement solaire sur le cuir n’a pas été suffisamment étudié jusqu’à présent. Dans le cadre de ce qui précède, la présente étude a été réalisée sur des échantillons expérimentaux de cuir hydrophobe et initiale (témoin) dans une zone ouverte pour déterminer l’influence du rayonnement solaire et des précipitations sur le cuir pour les tiges de chaussures. Au cours des tests, un examen systématique des échantillons exposés a été effectué pendant 1 à 6 mois, des échantillons ont été prélevés pour des tests physico-mécaniques et d’autres tests en fonction des conditions météorologiques. Après cela, les échantillons ont été soumis à une évaluation organoleptique, à des analyses physico-mécaniques et chimiques, ainsi qu’à des analyses structurelles. Il a été déterminé visuellement que, selon la variante hydrophobe utilisée, les formations de collagène fibrillaire changent de différentes manières. Après l’action du rayonnement solaire atmosphérique sur l’échantillon témoin, sa structure fibrillaire change brutalement, de nombreuses microfissures apparaissent, situées principalement perpendiculairement à l’axe des fibres et il existe des zones sombres bien définies entre les fibres. Les contours des fibrilles deviennent indistincts, de nombreuses extrémités cassées sont observées. Cependant, de tels changements ne sont pas observés dans le cas d’échantillons hydrophobes. Des changements importants dans les propriétés physiques et mécaniques sont observés au cours des premier et quatrième mois du vieillissement naturel. Dans le cas de l’échantillon hydrophobe, la vitesse d’évolution des dommages hydrothermaux et l’apparition de fissures dans la couche superficielle de l’échantillon soumis au vieillissement en zone ouverte est toujours plus faible par rapport à l’échantillon témoin.

MOTS CLÉS : dommages hydrothermaux, hydrophobie, rayonnement solaire, destruction, structure fibrillaire

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INTRODUCTION

Significant studies have investigated the effect of solar radiation on collagen-based materials [1-3]. Nalyanya *et al*. [4] have reported an investigation on the effect of artificial ultraviolet radiation on the viscoelastic and dynamic viscosity of both pickled and tanned leathers. However, to our knowledge, there appears no documented investigation into the effect of unfiltered solar radiation on the mechanical properties of bovine leather. Therefore, this study presents the results on effects of natural solar radiations on the viscoelastic properties of bovine leather using thermal and dynamic mechanical analyses. This investigation also reports the effects of oscillation frequency and furnace temperature on the viscoelastic properties of leather. The study also makes a comparison of the effect of solar radiation on tanned leather and pickled leather to explore the effect of chrome-tanning on the solar radiation absorption of bovine leather.

It is well known that the Republic of Uzbekistan is located in Central Asia and has a favorable economic as well as strategic location.

About 300 sunny days and less than 300 ml of rainfall are observed annually in Uzbekistan. The continental climate is expressed in sharp fluctuations in temperature day and night, in summer and winter. In summer, the average temperature exceeds 35°C, and on some days, it is even higher than 45°C. Heat is relative.

The average annual rainfall in the plains is about 90-580 mm, and in the mountains about 460-910 mm [5-6]. In the summer, the sun does not leave the sky for 300-330 hours per month in the north and 380-390 hours in the south. The largest solar radiation is observed on the flat territory of the Republic of Uzbekistan (annual amount of 6400 MJ/m^2) and is slightly reduced in the foothills, very easy to carry thanks to low humidity.

Cloudiness reduces the total radiation flux, and with continuous cloudiness direct radiation is absent. The regional potential of total solar energy can be characterized by the average annual value of solar radiation per $1m^2$ (cm^2) of horizontal surface.

To assess the duration of the flow of solar energy, a total indicator is used - the annual amount of sunshine. For Uzbekistan, it is 2815-2880. It may be noted that the effect of solar radiation on natural skin has not been sufficiently studied.

EXPERIMENTAL PART

When performing the work, the following were used: acrylic emulsion A-1, polyvinyl ethinyl dihydroxychlorosilane, industrial oil IA-20, penetrator and widely used polyethylhydrosiloxane. Based on them, a composition of water repellents was prepared in various initial ratios. Water repellents were prepared by sequentially mixing the above materials at a temperature of 20–22°C for 3-4 hours [7-8].

Studies of structural, physico-mechanical and physico-chemical properties, electron microscopy methods, and standard methods for assessing the properties of the materials were used.

Objects of Study

Polymethylsiloxane Liquids (PMS-100, PMS-200) are transparent, chemically inert liquids. They are a mixture of polymers of linear structure $(CH_3)_3Si\ [—OSi(CH_3)_2]n$, where n = 3-700. Density at a temperature of 20°C was in the range of 0.98-0.99 g/cm^3, boiling point 300°C, pour point 62-64°C.

A Surfactant Preparation (OP-10) (a mixture of ethoxylated dialkylphenols), $CnH_{2n+1}C_6H_4O\ (C_2H_4O)_m\ H$, where n = 9-10, m = 10-12, is a light yellow oily paste, the pH of the aqueous solution is 7-8. The clarification of the aqueous solution occurred at a temperature of 90°C [9].

Acrylic Emulsion №1 is an aqueous dispersion of polymethyl acrylate, plasticized during the polymerization with a small amount of dibutyl phthalate [10-11].

Polyvinylethinyldihydroxychlorosilane. In a four-necked flask with a volume of 500ml, equipped with a mechanical stirrer with a shutter, a thermometer, a dropping funnel and a reflux condenser, 103.78 ml (74 g 1.0 mol) of ethyl ether (or 88.73 ml (78 g 1.0 mol) of benzene). Then, 53.29 ml silicon tetrachloride were poured with stirring (85g 0.5 mol). After that, the temperature was raised to 60°C and 68.42 ml vinyl ethynyl magnesium bromide was added portionwise (77.5 g 0.5 mol) for 45-50 minutes. Then, with vigorous stirring, the temperature was raised to 70°C, the reaction continued for another 4.0-5.0 hours. After time, the stirrer was stopped, allowed to cool for 2.0 hours and cooled to 10.0 ± 2.0°C.

Then, in small quantities, the reaction mixture was transferred to a separatory funnel, washed several times with double-distilled water (until chlorine ions appeared in the washing water, with a breakdown with silver nitrate) to remove magnesium chloride.

Ethyl ether solvent was distilled off by vacuum distillation at a temperature of 35.6°C (or benzene at 80.1°C), using a vacuum pump, with a pressure for ethyl ether of 1.8-2.0, and in the case of benzene, 5.0-5.2 mm.

The resulting vinyl ethynyl trichlorosilane was introduced into the sump and 81.63 ml was released from there. Intermediate of 182.57 ml was added to the mixer with stirring of vinylethynyl trichlorosilane, water, for 2.0 hours at a temperature of 146 ± 5.0°C for the purpose of hydrolysis of the intermediate.

The hydrolysis of vinyl ethynyl dihydroxychlorosilane was done with 182.565 ml water for 2.0 hours in a temperature range of 146 ± 5.0°C.

Then the target product of vinyl ethynyl dihydroxychlorosilane was subjected to distillation, and the product was obtained PVEDGOHS with ethyl ether 75.46 ml (58%) in the case of benzene 70.60 ml (58%) [12].

Experimental Technique

Methodology for the Preparation and Use of Water Repellents

Production Technology. Water repellents were prepared by sequentially mixing the starting materials at various ratios (wt.%) As an experimental option: acrylic emulsion-20% 40-70, polyvinylethinyldihydrosichlorosilane-80% 2-12, industrial oil, IA-20 12-53, penetrator 4-6 and control polyethylhydrosiloxane (GKZh-94) 100 at a temperature of 20–22°C for 3-4 hours.

Technology Application. Application by plush brush: not diluted, or diluted in a 1:3 ratio. Spraying: diluted in an aqueous medium in a ratio of 1:2 is sprayed in 1-2 passes from a distance of 20-30 cm. It should be noted that the action of the hydrophobizing composition occurs immediately after the complete evaporation of the solvent. Liquid formulations do not change the tone of dyed skin.

Methodology for Studying the Properties of Water Repellents

Determination of Skin Steam. The steam capacity of the skin was estimated by the amount of moisture absorbed by the sample, in % of the mass of an absolutely dry sample:

$$P = \frac{a-b}{b} \cdot 100, \qquad (1)$$

where, a is the mass of the sample after absorption of moisture, g; b is the mass of an absolutely dry sample, g [11].

Determination of Breathability. Breathability is determined on the basis of Interstate standard GOST 938.18-70. This standard applies to all types of skin and establishes a method for determining breathability. A device was used to determine breathability.

The breathability of the skin and skin tissue of the fur characterizes their ability to pass air at a pressure difference on both sides of the test sample.

The air permeability index, $cm^3/(cm^2 \bullet h)$, is the air volume in cubic centimeters passing through 1 cm^2 of the test sample for 1 h with a pressure difference on both sides of the sample equal to 9.81 MPa. The results of the absolute breathability test B_a, s, were calculated by the formula:

$$B_a = t - t_0 \qquad (2)$$

where t is the time taken to pass 100 cm^3 of air, s; t_0 is the outflow time of 100 cm^3 of water from the device without a sample, s.

The final result was calculated as the arithmetic mean of two definitions. Relative breathability was found by the formula: $B_0=V \bullet 3600/S$, B_a, where V is the volume of air passing through the sample (according to the test conditions it is equal to 100 cm^3); S is the working area of the sample, equal to 10 cm^2; B_a - absolute breathability, s. [12].

Water Permeability Tests in Static Conditions. Water resistance and permeability under static conditions are determined on the basis of Interstate standard GOST 938.21-71. This standard applies to all types of leathers and establishes a method for determining water resistance and permeability when testing leather samples in static conditions. Water permeability is characterized by the amount of water passing through a wet sample. Water permeability and permeability of skin samples were determined on a PVS-2 device.

To test the sample, 2 ml of water was passed through it (provided that it would take no more than 2 hours), after which the water level was noted on the graduated tube of the device with an absolute error of 0.05 ml and the time was recorded on the counter. Then, 5 ml of water was passed through the sample and its level in the tube and time were noted a second time. The water level and time were used to calculate the amount of water that passed through the sample for the corresponding time. When testing denser samples, first left under water pressure for 2 hours (during this time no more than 2 ml of water should pass through the sample), after which the water level in the tube and time were noted. Then the level was noted after 2 hours. If an insignificant amount of water passed through the sample in 2 hours, then the tests continued for another 2 hours. At least two determinations were made with each sample, the difference between them did not exceed 10% of the average value. The test shall be carried out at a temperature of 20 ± 2.0°C.

Water permeability, ml/(sm^2•h), calculated by the formula:

$$B=\frac{V\cdot 60}{t\cdot S} \qquad (3)$$

where, V is the amount of water passing through the sample during the test, ml; t is the test time, s; S is the sample area, cm^2 [9].

Determination of Vapor Permeability. Vapor permeability is determined on the basis of Interstate standard GOST 938.17-70. This standard applies to all types of skin and establishes a method for determining vapor permeability. The following equipment and reagents are used to determine vapor permeability: technical scales in accordance with Interstate standard GOST 24104-2001; desiccators according to Interstate standard GOST 25336-82 with an inner diameter of 250mm; metal glasses 45mm high and 55mm in diameter.

Vapor permeability is the ability of the skin to pass water vapor. Vapor permeability is one of the most important indicators used to assess the hygienic properties of the skin. Vapor permeability is expressed in milligrams of moisture passing through 1 cm^2 of sample area in 1 h, or as a percentage of the mass of water vapor passing through the test sample to the mass of water evaporated from an open surface under the same conditions.

Vapor permeability was determined in special metal cups on round samples with a diameter of 55 mm; the diameter of the working part of the sample is 36 mm.

The relative vapor permeability P_0, %, was calculated by the formula:

$$P_0=\frac{q\cdot 100}{q_1} \qquad (4)$$

where, q is the decrease in mass of the glass with the contents after 6 hours of testing, g; q_1 is the arithmetic mean of the decrease in the mass of control glasses with water, g.

In the case of vapor permeability of the samples, P must be expressed in milligrams of moisture passing through the unit area of the sample per unit time, then the calculation was performed according to the formula:

$$P_0=\frac{q}{t\pi r^2} \qquad (5)$$

where, q is the decrease in mass of the glass with the contents, mg; t is the duration of the experiment, h; πr^2 is the working area of the sample, cm^2. The arithmetic average of the test results of two samples taken from the same sample was taken as the test results [12].

Determination of Hygroscopicity. Hygroscopicity also characterizes the ability of the skin to absorb water vapor from the surrounding air. The hygroscopicity of the samples was determined by increasing the mass of the sample, maintained at a relative humidity of 100% for 16 hours, and expressed as a percentage of the initial mass of the sample.

Tests are carried out on samples with dimensions of 50 × 50 mm.

Samples aged under normal atmospheric conditions were weighed on an analytical balance with an absolute error of 0.001 g and placed in a desiccator above water so that they had free air access.

The relative humidity above the water in the desiccator was 100%. After 16 hours in a desiccator, the samples were weighed and the hygroscopicity *G*, %, was calculated by the mass gain referred to the mass of the air-dry sample:

$$G = \frac{q_1 - q_2}{q} \cdot 100 \qquad (6)$$

where, q_1 is the mass of the sample moistened in a desiccator, g; q_2 is the mass of the same sample in the air-dry state, g [9].

RESULTS AND DISCUSSION

During the tests, a systematic examination of the exposed samples was carried out, sampling for physico-mechanical and other tests, while meteorological conditions were recorded.

The control and experimental hydrophobized samples were taken at certain intervals during their stay in atmospheric conditions (1-6 months). Figure 1 shows the corresponding photographs [14-15].

Figure 1. Photographs of experimental and control hydrophobized samples produced during (a-January, b-June) 6 months of their stay in atmospheric conditions

The studies were carried out on 5 longitudinal and 5 transverse control and experimental samples of chrome tanned leather for upper shoes.

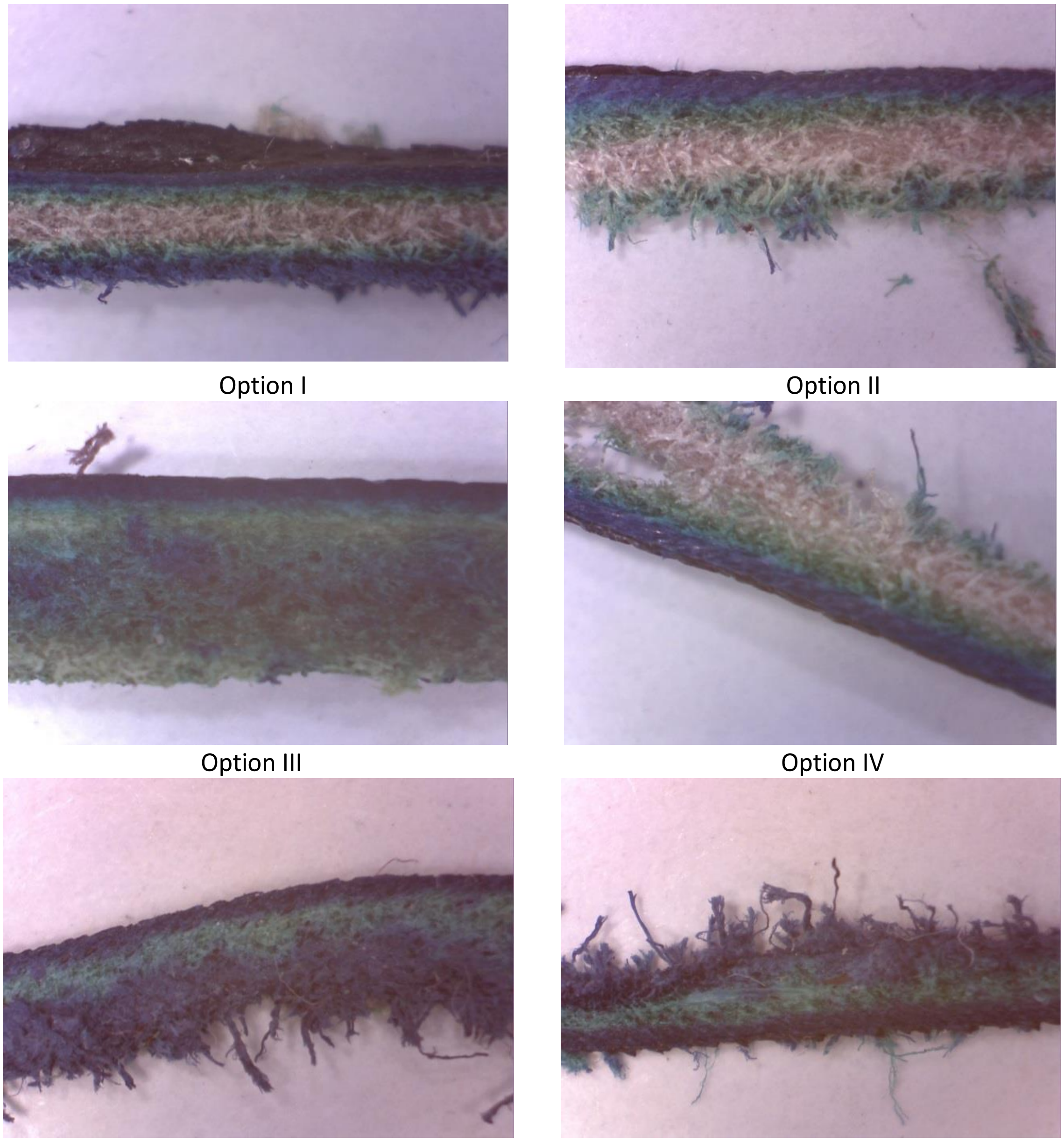
It should be noted that when examining the skin (Fig. 2) after exposure to harsh climatic factors, changes in their color, structure and the appearance of micro cracks were noticed.

The results of microscopic studies showed that the characteristic properties of the leather for the upper of chrome tanning shoes are reflected in their structure. The results of microscopic studies showed that the characteristic properties of the leather for the upper of chrome tanning shoes are reflected in their structure.

It was visually determined that, depending on the variant of hydrophobization used, fibrillar collagen formations change in different ways.

After atmospheric insolation acts on the control sample, its fibrillar structure changes sharply, numerous micro cracks appear, located mainly perpendicular to the fiber axis, and clearly defined dark zones are found between the fibrils. The contours of the fibrils become indistinct, there are numerous torn ends.

However, such changes are not observed for hydrophobized samples. In the control variant, an increase in the number of cracks was noted and the surface becomes rough.



Option I

Option II

Option III

Option IV

Option V

Option VI

Figure 2. Microscopic photographs of experimental (I-IV) and control (V) skin samples (Magnification × 200 times)

It must be emphasized that the process of destruction of the surface of the skin proceeds mainly under the influence of the above photochemical effects caused by ultraviolet rays [16-17].

The test results further show that the longer the insolation of solar radiation with alternating precipitation lasts, the more the breaking stress and the hydrothermal degradation of chrome tanned leather for the upper of the shoe decrease. It was determined that the hydrothermal degradation of the skin and the tensile stress change according to a certain regularity: a decrease in hydrothermal degradation and a weakening of the tensile stress. As a result of exposure to natural factors, the skin gradually loses its strength properties [18-19].

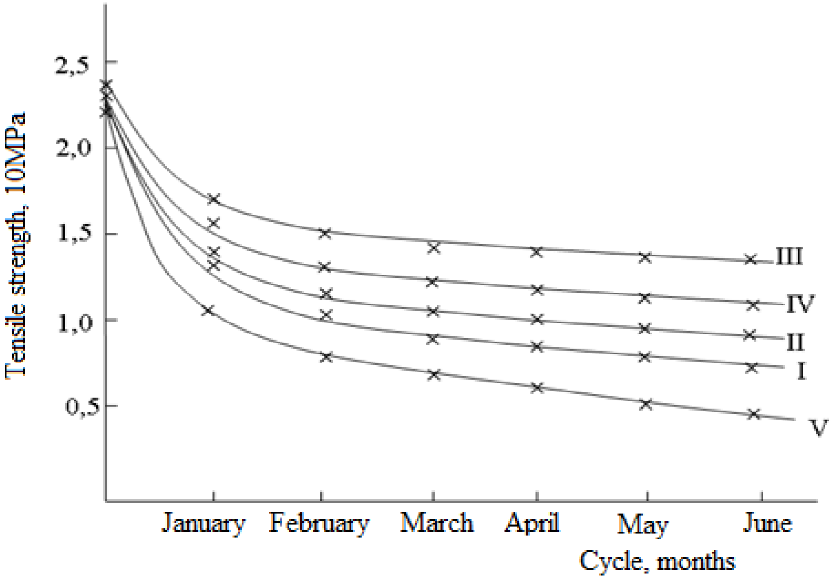


Figure 3. The dependence of the tensile strength of the skin treated with various options of water repellents on the duration of exposure climatic factors: I-IV experimental and V control skin sample

An intensive change is also observed in the case of aging under the direct influence of solar radiation and precipitation. In Fig. 3. curves of the tensile strength of skin samples treated with water repellents on the duration of exposure to climatic factors are presented: I-IV experimental and V control skin samples.

As revealed, in the control V version, the tensile strength decreases sharply in comparison with I-IV experimental versions of hydrophobized samples. Moreover, in all cases, the maximum decrease from 2.20 to 2.65 *MPa*, the tensile strength drops 1.64-0.75 *MPa* from January to March. Further, in the following months, the value of this indicator will be in the range of 0.42-193 *MPa*. In these cases, maximum strength is observed for the III - hydrophobized skin sample. Among environmental factors, solar radiation has a significant effect on the properties of leathers for chrome tanned shoe uppers. It speeds up the aging process. In Fig. 3. the change in elongation of I-V skin samples is shown, both initial and modified using hydrophobic composite materials.

From the results obtained, a strong decline in elongation of the samples was observed in the first four months. It should be noted that the III experimental skin sample has a maximum elongation of six months compared with other samples, and the minimum as expected for V control sample. Their difference, i.e. elongation is about 10%, which once again confirms the high hydrophobizing ability of the studied objects for resistance to environmental factors.

In studies, the influence of atmospheric effects on the facial surface of the skin and on hydrothermal stability was simultaneously studied. With a few exceptions, it was found that natural aging, along with mechanical and physical properties, reproduces well the changes in such indicators as the appearance of cracks in the face layer under tension, and hydrothermal stability.

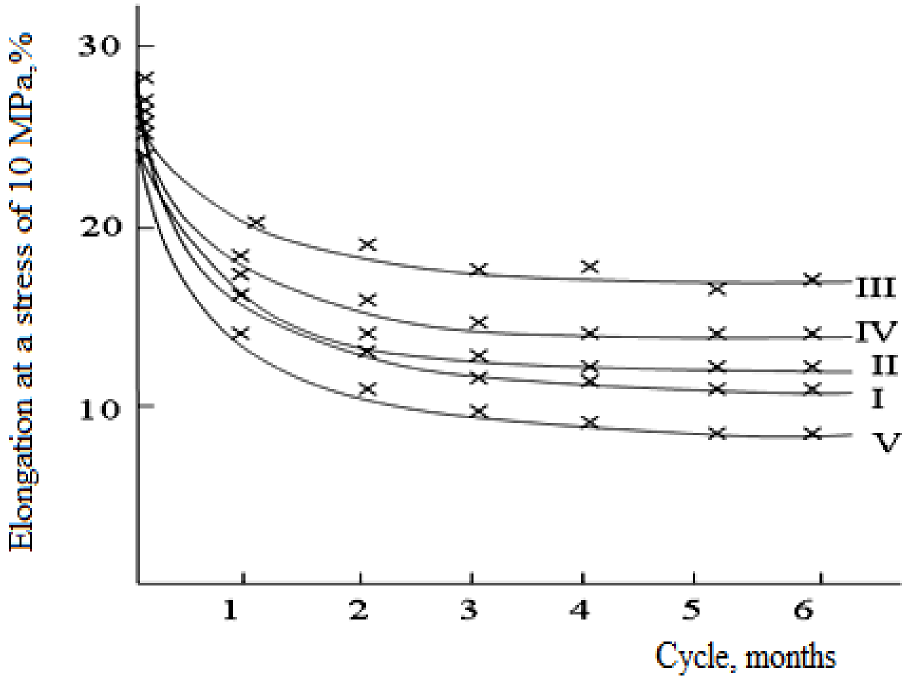


Figure 4. Change in skin lengthening for treated with various variants of water repellents on the duration of exposure to climatic factors: I-IV experimental and V control sample of the skin

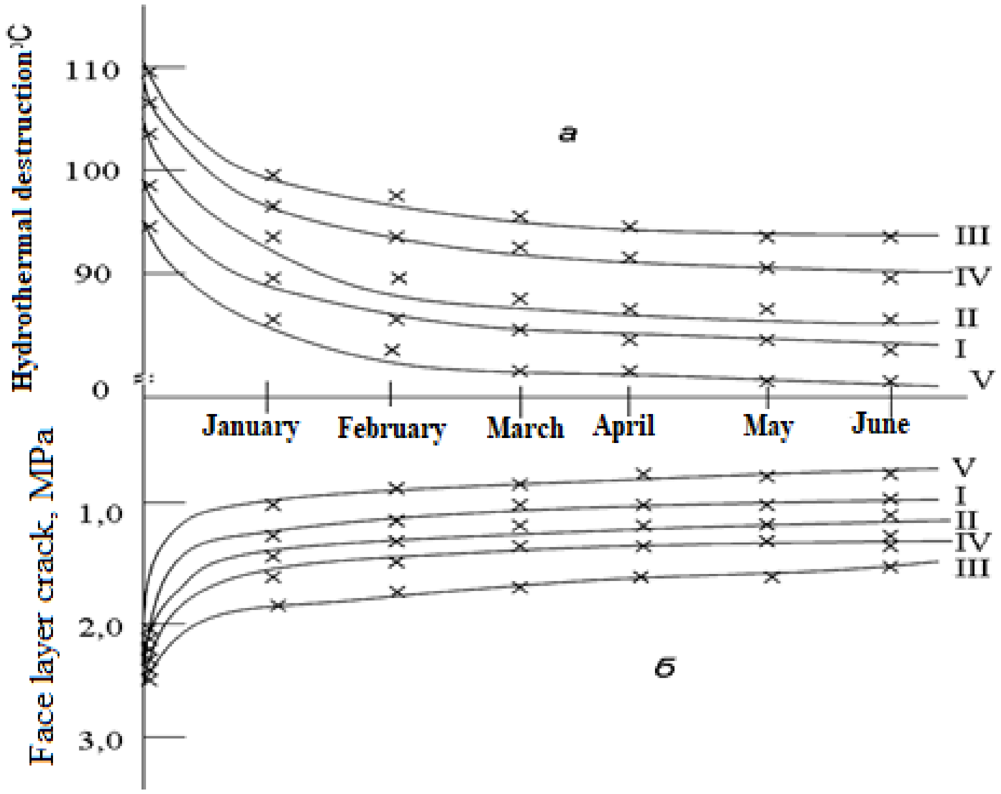


Figure 5. Kinetic dependences of hydrothermal destruction (a), and the appearance of cracks in the facial layer of the skin (b) treated with various variants of water repellents on the duration of exposure to climatic factors: I-IV experimental and V control skin samples

Fig. 5. kinetic dependences of hydrothermal destruction (a), the appearance of cracks in the facial layer of the skin (b) treated with various types of water repellents on the duration of exposure to climatic factors are given: I-IV experimental and V control skin samples.

The results of the kinetic dependences of hydrothermal destruction and the appearance of cracks in the facial layer of the skin treated differently with the help of water repellents on the duration of exposure to climatic factors and the control skin sample are corrected to a certain extent with previously obtained data.

Significant changes in physical and mechanical properties are observed in the first and fourth months of natural aging. In the third sample, the rate of change in hydrothermal destruction and the appearance of cracks in the face layer subjected to aging in an open area, is always lower compared to the control sample. It also seemed very important to study the chemical composition of experimental hydrophobized and control skin samples. In Table 1 the results of chemical analysis of experimental and control hydrophobized skin samples are presented [20].

Table 1: Chemical analysis of experimental and control hydrophobized leather samples

		Options					
		Experienced					
	Indicator	I	II	III	IV	V	Control Interstate standard GOST 338-81
Content, %:	Chromium oxide	3.2	3.4	3.6	3.7	2.8	n/l 4.3
	Silica	2.3	2.4	2.6	2.8	2.4	n/l 1.8
	Ash	1.5	1.8	2.0	2.2	2.4	n/m 3.3
	Substances extracted with organic solvents	10.5	11.7	11.5	12.3	10.2	10-13
	Water washed common	2.3	2.4	2.4	2.6	3.4	n/l 4.2
	Fatty substances	34.3	26.1	28.9	26.6	20.4	n/l 23.4
	The number of products, %	25.5	31.9	41.9	29.3	26.4	n/l 36.7

From the data of table 1, as can be seen, with an increase in the content of polyvinyl ethyl dihydroxychlorosilane in the experimental variants, the contents of chromium oxide and silicon dioxide increase accordingly [21-22]. You can also notice a slight increase in the relative content of ash and substances extracted with organic solvents. A change in the components of the skin leads to a change in the number of products. In experimental skins, the product number the average for all options was 32,15%, which is within 20% more compared to the control. It also seemed very important to carry out the spectroscopic study of the interaction of hydrophobizing compositions with collagen.

The aim of this work is to study by IR spectroscopy the nature of the bonds of the studied hydrophobizing composites with the main skin protein, collagen. Measurements of IR spectra were carried out on a Specord 75IR spectrophotometer made in Germany [23-24].

Collagen was used as a model. The object of the study was a film obtained from a 4% collagen solution, hardened by immersion in a solution of tanning chromium compounds with a basicity of 45% and a Cr_2O_3 concentration of 100g/l for 1 hour, then followed by drying and rinsing. After obtaining the film, its absorption spectrum in the IR region was determined and subjected to treatment with the investigated hydrophobizing agents: a hydrophobizing composition based on PVEDHOHS, an emulsion of polyethylhydrosiloxane and collagen.

IR spectra of the studied preparations were recorded using high-resistivity silicon wafers as a substrate. The spectrum of the organosilicon liquid of polyethylhydrosiloxane was recorded using a sample in the form of a layer between plates on NaCl.

The manifestation of the hydrophobic properties of the hydrophobizing composition is based on the hydrolysis reaction of the chromium complex of stearic acid. Moreover, the molecules of the hydrolyzed substance, reacting with each other, form difficultly soluble high-molecular products that are firmly held by the material.

Comparison of the spectra of the initial and treated PVEDOHS with collagen and polyethylhydrosiloxane with collagen, Fig. 6-7.

In the range of 3600-3100 cm^{-1}, a stretching vibration of OH and NH groups appears by bonded hydrogen bonds.

Stretching vibration (Vk) of CH, CH$_2$ groups appears in the region of 2980 and 3100 cm^{-1}.

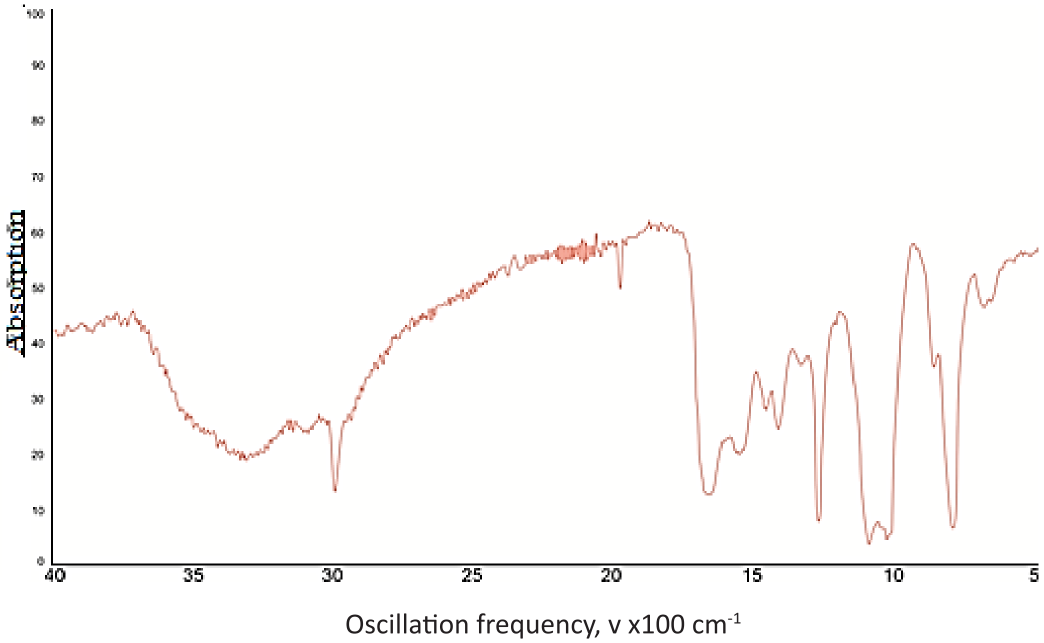


Figure 6. Spectrum III version of the prototype

In the range of 3500-3055 cm^{-1}, a stretching vibration of OH and NH groups by hydrogen bonding appears, Figure 6. Stretching vibration (Vk) of CH, CH$_2$ groups appears in the range of 2990 and 3090 cm^{-1}. Carbonyl group (C=O) Amide I appears in the 1660 cm^{-1} region. The deformation NH-bond appears at 1550 cm^{-1}. The deformation CH, CH$_2$ appears in the region of 1450 and 1410 cm^{-1} and in the OH group. The absorption band of Si(CH$_3$) appears in the region of 1270 cm^{-1}, Si-O bonds with an open chain appear in the region of 1090-1025 cm^{-1}, and Si(CH$_3$) bonds appear at 800-790 cm^{-1}. Carbonyl group (C=O) Amide I appears in the region of 1650 cm^{-1}. The deformation NH-bond appears at 1530 cm^{-1}.

Deformation CH, CH$_2$ appears in the region of 1450 and 1400 cm^{-1} and in the OH group. The absorption band of Si(CH$_3$) appears in the region of 1270 cm^{-1}, Si-O bonds with an open chain appear in the region of 1090-1010 cm^{-1}, and Si(CH$_3$) bonds appear at 790-780 cm^{-1}.

When comparing the IR spectra of collagen treated with polyethylhydrosiloxane and collagen in the presence of a zirconium salt, one can see insignificant absorption bands at 2160 and 830 cm^{-1}, characteristic of stretching and bending vibrations of the Si-H bond, as well as an expansion of the absorption band in the region of 3380-3280 cm^{-1}, which can be explained by the adsorption of silicone both on the collagen surface due to the forces of intermolecular attraction between the polar collagen groups and the Si-O dipole, and on the catalyst surface. The possibility of the formation of hydrogen bonds with the amino groups of collagen with the participation of the Si-H – groups of polyethylhydrosiloxane is not excluded (Fig. 7).

The IR spectrum of the original collagen shows all absorption bands characteristic of collagen, since the constituent of collagen is proteins and amino acid residues.

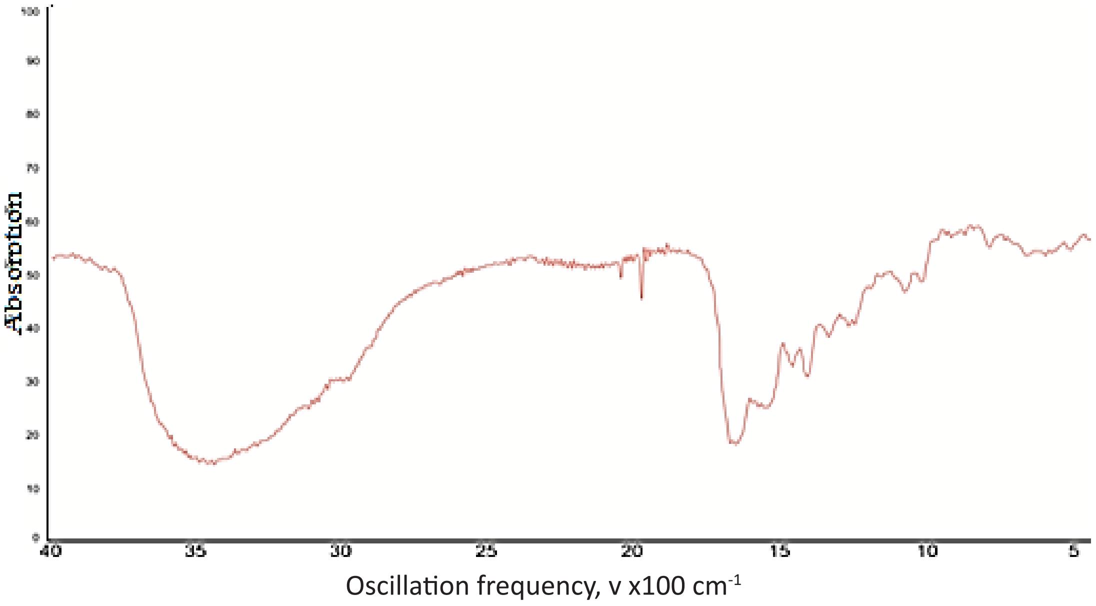


Figure 7. VI-variant, the original sample of collagen

Thus, we can conclude that a comparison of the spectra of the initial and processed collagen with PVEDOHS shown in Fig. 6-7 shows a significant broadening of the absorption band in the region of 3500-3100 cm^{-1} and a noticeable increase in the intensity of the CH, CH_2 group at 2980 cm^{-1}.

In accordance with the blurring and broadening of the bands of stretching vibrations of hydroxyl groups in this region, this suggests the presence of a hydrogen bond between the OH groups of the hydrolyzed complex and the functional NH- groups of collagen. However, the interaction of the chromium complex with the amino groups of collagen is also possible with the formation of strong covalent bonds between the nitrogen and chromium atoms.

When studying the IR spectra of PVEDHOCS, a certain shift of the absorption band was observed, sometimes it shifts somewhat towards lower frequencies. The presence of absorption bands at 1400, 1375, 1235 cm^{-1} corresponds to the C-C bond. The shift of the band in the region of 3460, 3400, 3280 cm^{-1} corresponds to the stretching vibrations of OH groups.

In this case, the characteristic bands for the ethylene bond are found in the frequency range 1600, 1530 cm^{-1}; an absorption band is present in the spectra of the PVEDOHS compound. At 600, 550 cm^{-1}, a band characteristic of Si-Cl is observed.

Absorption bands in the frequency range 1650, 1550 and 1450, 1414 cm^{-1} remain unchanged from the IR spectra of collagen treated with PVEDGOHS. This is characteristic of the COOH groups of collagen, indicating that during the adsorption of the complex, it can decompose into water-insoluble basic chromium stearate and water-soluble chromyl chloride, which has a tanning effect.

That the organosilicon liquid polyethylhydrosiloxane in the form of an emulsion is fixed on collagen only through the forces of a sorption nature and does not form strong covalent chemical bonds with collagen.

It was found that the spectrum of processed collagen does not differ in any way from the spectrum of untreated collagen, which leads to the conclusion that there is no noticeable chemical interaction between polyethylhydrosiloxane and collagen under these conditions.

CONCLUSIONS

The results of the study carried out in the IR spectrum give reason to believe that the effect of hydrophobization, in the case of using various composites, is due to the interaction of the hydrophobizator with the functional groups of collagen, a certain orientation of hydrocarbon radicals, the formation of a water-repellent film, as well as a combination of these processes.

Conducting comprehensive studies on the aging process has established that when exposed to chrome skins, the effects of sunlight, oxygen, temperature, air humidity and precipitation jointly affect them.

It is known that aging of polymers under the action of sunlight is a photochemical process. In this case, the polymer molecules, first absorbing a quantum of energy of the corresponding wavelength of light, goes into a highly excited state. After that, either the molecule gives up energy in the form of a light quantum, or spends its energy on the oxidation and destruction reactions. This explains the greatest decrease in breaking stress and breaking load when exposed to solar radiation on the control samples.

Based on this, it can be concluded that hydrophobizing compositions based on polyvinylethinyldihydroxychlorosilane, especially the III experimental version, are the most effective.

The obtained results of the experiments clearly demonstrated that insolation of solar energies and precipitation cause a complex of physicochemical transformations. Such processes occur at a fairly high speed under the influence of oxygen, ozone and other gases, as well as solar radiation, heat and humidity. The nature of the ongoing processes is significantly affected by hydrophobic compounds containing in skin products. Thus, aging and skin destruction processes are prevented.

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