Diffusion of a hydrophobisis composition in the structure of chrome skin and the influence of them on hygienic properties

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Abstract. The main results of the study of the diffusion of the hydrophobic composition in the structure of chrome leather for the upper of the shoe are presented. In our work, the main objects for research were: acrylic emulsion A-1, polyvinyl ethinyl dihydroxychlorosilane, industrial oil IA-20, penetrator and widely used polyethyl hydrosiloxane. 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. When studying the effect of the mass fraction of polyvinyl ethinyl dihydroxychlorosilane mixed with synthetic polymers on the viscosity of systems, it was found that all obtained with increasing temperature have a smooth decrease in viscosity. The increase in the viscosity of the mixture is explained by the fact that a significant amount of halogen and hydroxyl groups contained in the polyvinyl ethinyl dihydroxychlorosilane macromolecules apparently contribute to the formation of sufficiently strong intermolecular bonds between the individual components in which aggregation can occur, with the formation of composite compounds. The experiments also indicate that the samples, previously moistened with a control water repellent, have a higher value of the moisture absorption index. However, after 6-10 cycles, this indicator of skin samples, previously moistened with water, gradually stabilizes. This is obviously due to the fact that water in subsequent processes in contact with the skin form rather strong bonds with the structural elements of the dermis. Therefore, the wetness of chrome leather for the upper of the shoe is reduced, as a result of which the water resistance of the upper of the shoe is increased.

1. Introduction

Natural leathers have valuable properties: good breathability, water vapor permeability and thermal conductivity, compares favorably with other materials with durability and elastic properties. However, the skin has significant disadvantages: high water permeability, lack of resistance to water.

Purpose of work: is the creation of a more affordable and effective hydrophobic composite material based on new and local compounds.

The creation of finishing coatings for waterproof leather is a complex task. Technologists for dressing and finishing leather should develop production technology in close cooperation and correctly select materials for liquid and finishing processes. Thanks to the fibrous structure, the skin and its products easily absorb moisture. Wet skin loses its heat-shielding properties and vapor permeability, easily undergoes rotting and mold. After drying, the skin becomes tough, brittle, its bending strength decreases.
The purpose of hydrophobization is to improve the operational properties of the skin without compromising hygienic properties (breathability, vapor permeability). In addition, it is desirable that the hydrophobic effect does not decrease during the operation of leather products for a long time.

One of the most promising and effective methods of imparting water-repellent properties to the skin is the treatment of it with organosilicon oligomeric products. High hydrophobicity of the skin is achieved by treating it with siloxanes in organic solvents. The skin can be treated by spraying or applying a siloxane coating with a brush or spray [2].

In the current article, the possibilities of obtaining new water repellents and their application in the skin finishing technology were investigated on various chemical materials and systems. For this purpose, various natural film-forming agents, film-forming polymers, plasticizers and other auxiliary materials were used in this work.

2. Objects of study
Polymethylsiloxane liquids (PMS-100, PMS-200) are transparent, chemically inert liquids. They are a mixture of polymers of linear structure \( (\text{CH}_3)_2\text{Si}[\text{O}]—(\text{CH}_3)_2\text{Si}_n \), 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) \( \text{C}_6\text{H}_{3n-1}\text{C}_6\text{H}_2\text{O}((\text{C}_2\text{H}_4\text{O})_{10} \text{H} \), 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 [3].

Acrylic emulsion No. 1 is an aqueous dispersion of polymethyl acrylate, plasticized during the polymerization with a small amount of dibutyl phthalate [4].

Polyvinylethynylidi hydroxychlorosilane [5]. In a four-necked flask with a volume of 500\( \text{ml} \), equipped with a mechanical stirrer, a thermometer, a dropping funnel and a reflux condenser, 103.78 \( \text{ml} \) (74 g. 1.0 \( \text{mol} \)) of ethyl ether (or 88.73\( \text{ml} \). (78 g. 1.0 \( \text{mol} \)) of benzene). Then, 53.29 \( \text{ml} \) were poured with stirring. (85g. 0.5 \( \text{mol} \)) Silicon tetrachloride. After that, the temperature was raised to 60°C and 68.42 \( \text{ml} \) was added portionwise. (77.5 g. 0.5 \( \text{mol} \)) Vinylethynyl magnesium bromide 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 amounts, 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 \( \text{ml} \) was released from there, intermediate in the mixer. 182.57 \( \text{ml} \) was added to the mixer with stirring of vinylethynyltrichlorosilane. water, for 2.0 hours at a temperature of 146 ± 5.0°C for the purpose of hydrolysis of the intermediate.

The hydrolysis of vinylethynylidi hydroxychlorosilane was 182.565 \( \text{ml} \). water for 2.0 hours in a temperature range of 146 ±5.0 °C.

Then, the target product of vinylethynyldihydroxychlorosilane was subjected to distillation, and the product PVEDHOCHS with ethyl ether was obtained 75.46 \( \text{ml} \) (58%) in the case of benzene 70.60 \( \text{ml} \) (58%) [6].

3. Research methodology
3.1. 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, polyvinyl ethinyl
dihydrosichlorosilane-80% 2-12, industrial oil, IA-20 12-53, penetrator 4-6 and control polyethyl-
hydrosiloxane (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.

3.2. Methodology for studying the properties of water repellents
Viscosity: to determine the viscosity of sample solutions, methods were used based on measuring the 
flow rate of a certain volume of liquid through a capillary, as well as measuring the resistance provided 
by a solution of a certain concentration.

3.3. Determination of conditional viscosity of water repellents
To determine the viscosity of water repellents, aqueous solutions of standard concentration were 
prepared. A standard is considered to be a 14.82% solution of water repellent (GOST 3252-80) in terms 
of anhydrous and ashless products [7].

It has been established that the determination of the conditional viscosity of the studied water 
repellents is conveniently determined on a VZU viscometer, because changing the diameter of the fluid 
passage on the indicated 
viscometer a wide range of definitions.

The nominal viscosity of the tested water repellent (0.4)E20 was calculated by the formula:  

\[ B_v = \frac{t_1}{t_2} \]

where \( t_1 \) is the expiration time of water repellents at a temperature of 40 °C; \( t_2 \) - time of water outflow 
at a temperature of 20 °C.

The viscosity was calculated with an error of not more than 0.1 about. The discrepancy between 
parallel determinations did not exceed 0.1%.

3.4. Determination of the density of water repellents by the pycnometric method.
The density \( P_{4}^{20} \) was calculated by the formula:

\[ P_{4}^{20} = \frac{(m_1 - m)}{V} \]

Where, \( m \) - is the mass of the empty pycnometer, g; \( m_1 \) - is the mass of the pycnometer with the 
analyte, g; V - is the volume of the pycnometer determined by calibration, sm³ [7].

Sorption properties of the samples — the study was carried out on a Mc-Ban vacuum balance with a 
quartz spring, in the range from 0-100% relative humidity, at 25°C.

3.5. Water permeability tests in static conditions
Water resistance and permeability under static conditions are determined on the basis of 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 was determined on a PVS-2 device.

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

\[ B = \frac{60V}{t \cdot S} \]

where, V - is the amount of water passing through the sample during the test, ml; t- is the test time, s; S-
is the area of the sample, sm² [7].

Water permeability tests in dynamic conditions: water resistance and permeability in dynamic
conditions is determined on the basis of GOST 938.22-71. This standard applies to all types of yufti and chrome leathers for upper shoes and establishes a method for determining water resistance and permeability when testing leather samples in dynamic conditions. Water and permeability of skin samples determined on the device PVD - 2.

Sorption properties of the samples — the study was carried out on a Mc-Ban vacuum balance with a quartz spring, in the range from 0-100% relative humidity, at 25°C.

4. Results and discussion
To obtain the required technological effect, from the use of two or more water-soluble polymers, in addition to the correct choice of components, their initial ratios in the resulting composites are important, which significantly affects the properties of the processed materials for leather products.

In this regard, the aim of our work was to study the properties of composites based on acrylic polymers and polyvinylethynylidi hydroxychlorosilane, which are of interest as water-repellent finishing materials [8-9].

In the work, the main objects for research were: acrylic emulsion A-1, polyvinylethynylidi hydroxychlorosilane, industrial oil IA-20, penetrator and widely used polyethyl hydrosiloxane. 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.

To determine the viscosity of sample solutions, methods were used based on measuring the flow rate of a certain volume of liquid through a capillary, as well as measuring the resistance provided by a solution of a certain concentration.

To determine the viscosity of water repellents, aqueous solutions of standard concentration were prepared. It has been established that the determination of the conditional viscosity of the studied water repellents is conveniently determined on a VZU viscometer, because changing the diameter of the fluid passage on the indicated viscometer a wide range of definitions.

The compatibility of the starting components was evaluated by experimentally obtained data. Figure 1 shows the effect of temperature on the viscosity of solutions of experimental and control samples of water repellents, with their various initial ratios.

![Figure 1](image)

Naturally, as expected, the viscosity of the hydrophobizing solutions decreases with increasing temperature. When studying the influence of the mass fraction of polyvinyl ethynyl dihydroxychlorosilane mixed with synthetic polymers on the viscosity of systems, it was found that all the obtained dependences have a smooth decrease in viscosity with increasing temperature.

It also seemed very important to study the spectroscopic study of the interaction of hydrophobizing compositions with collagen [10].
For the objects studied in the work, there were also studies by UV spectroscopy of the nature of the bonds of the studied hydrophobizing composites with the main skin protein – collagen [11].

Measurements of UV absorption spectra were carried out on specord UV spectrophotometers Germany. 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$_2$O$_3$ concentration of 100g/l for 1 hour. Then followed by drying and rinsing. After obtaining the film, its absorption spectrum in the UV region was determined and subjected to treatment with the investigated hydrophobizing agents: a hydrophobizing composition based on PVEDHOCS, an emulsion of polyethylhydrosiloxane and collagen.

The absorption of electromagnetic radiation in the UV, visible and IR regions of the spectrum is quantitatively described by the Bouguer-Lambert-Beer law.

According to the physical nature of absorption bands in the UV region, they are associated with electronic transitions: when a molecule absorbs electromagnetic radiation in the UV region, a transition occurs between the electronic levels of the molecule.

Different electronic transitions require different energies, so the absorption bands are located at different wavelengths. The presence in the structure of single bonds (–C–C–) and isolated chromophore groups (–N = N; –N = O, etc.) causes absorption in the far UV region (100–200 nm). However, absorption in the far UV region (up to 200 nm) has no analytical value, since modern spectrophotometers operate in the spectral range starting from 180–200 nm.

Chromo forms are mostly groups of atoms with unsaturated bonds. However, polyethylhydrosiloxane and a composite based on PVEDOHS containing unsaturated C = C bonds absorb only in the spectral range > 200. The ethynyl group —C ≡ C— in the samples of variant I has a wide band up to 230 nm.

A wide diffuse band is also found in the region of 180-165 nm and two systems of bands, Ryberg series, in the region of 152-105 nm. Further, the presence of conjugations of two double bonds between carbon atoms was established, which leads to the appearance of intense absorption in the region of 225 nm.

It is known that the C-C bond between carbon atoms usually absorbs only in the long ultraviolet region. So, absorption spectra are observed, respectively, in the region of PVEDHOHS 135 nm.

Also, the absorption band of the chromophore group, depending on the conditions in which the chromoform is located (neighboring atoms, solvent, etc.), can shift within some limits.

For the purposes of spectrophotometric analysis, electronic transitions of conjugated π bonds are used. Conjugation causes the splitting of π-orbitals, which leads to the appearance of sublevels, the transitions of electrons on which require much less energy. In this case, absorption is shifted to longer wavelengths of the spectrum and has a high intensity.

Thus, in the UV-region, molecules that have in their structure conjugated chromophore groups absorb. The longer the conjugation system, the longer the spectrum absorbs the substance.

As we know from the literature, the most probable transitions in the UV-visible region belong to phenylalanyl, prolyl, histidyl, glycyl, glutamyl and methionyl, as a result of which they are predominantly determining the fluorescent properties of collagen, spectrally significant.

In variant III of experimental hydrophobized samples, the ethynyl group —C ≡ C— in the samples has a broad band up to 215 nm.

A wide diffuse band is also found in the region of 185-180 nm and two systems of bands, Ryberg series, in the region of 175-165 nm. Further, the presence of conjugations of two double bonds between carbon atoms was established, which leads to the appearance of intense absorption in the region of 230 nm. It is known that the C-C bond between carbon atoms usually absorbs only in the long ultraviolet region.

So, absorption spectra are observed, respectively, in the regions of PVEDHOHS 185 nm.
The absorption bands of the spectra with a maximum at 188nm can be explained by the fact that in the covalently saturated compound (PVEDOHC) containing a chlorine heteroatom, along with \( \gamma \)-electrons, there are p-electrons pairs. In this regard, it can be concluded that the electronegativity increases from left to right, causing a stronger binding of electrons, as a result of which (I_{max}) the wavelength shifts towards shorter wavelengths. CH\(_2\) = CH— 215-230 nm.

In variants V of experimental hydrophobized samples, the ethynyl group —C ≡ C— in the samples has a wide band up to 208 nm. There is also a broad diffuse band in the 195-180 nm region and two systems of bands, Ryberg series, in the 170-155 nm region. Further, the presence of conjugations of two double bonds between carbon atoms was established, which leads to the appearance of intense absorption in the region of 210 nm (figure 3).
It is known that the C - C bond between carbon atoms usually absorbs only in the long ultraviolet region.

So, absorption spectra are observed, respectively, in the regions of PVEDOHS -170 nm. The absorption bands of the spectra with a maximum in the region of 175 nm can be explained by the fact that in the covalently saturated compound (PVEDOH) containing a chlorine heteroatom, along with γ-electrons, there are p-electron pairs.

In this regard, it can be concluded that the electronegativity increases from left to right, causing a stronger binding of electrons, as a result of which (\(l_{max}\)) the wavelength shifts towards shorter wavelengths. \(\text{CH}_2 = \text{CH}\)– 210-220 nm.

![Figure 4. UV - spectrum, VI version of the control sample (Collagen).](image)

In the VI variants of the control samples (figure 4). It was found that the spectrum of treated collagen does not differ in any way from that of untreated collagen, which leads to the conclusion that there is no noticeable chemical interaction between polyhydrosiloxane and gelatin under these conditions. Further, it was necessary to clarify the role of additives in the process of achieving improved hydrophobic properties of the skin.

Experiments have shown that collagen has absorption bands in the UV region that are associated with the carboxyl group COOH and the NH group (instead of \(\text{NH}_2\)) adjacent to each other, since they are part of the cyclic fragment.

In addition, the probability of directed energy transfer from short-wavelength to long-wavelength absorbing centers in heterocyclic compounds correlates with the probabilities of the corresponding electronic transitions. In turn, the probability of going to 425nm is higher than to 291nm. Thus, a directed singlet-singlet energy transfer is possible in a collagen molecule.

The results of this study give reason to believe that the effect of hydrophobization, in the case of using various drugs, is due to the interaction of the drug 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.

From the spectra (figure 4) it can be seen that for collagen in the region from 200nm to 325nm, various electronic transitions are observed, of oxygen and nitrogen atoms, which are associated with transitions of unshared electrons from the ground state to antibonding orbits, as well as \(\pi-\pi^*\) transitions in conjugate links. In the samples, with an increase in the composition of PVEDHOCS, a shift of the absorption band to longer wavelengths is observed.
A characteristic absorption maximum at 285 nm was found by UV spectroscopy in callogen hydrolysates treated with hydrophobizing compositions based on PVEDOHCS. This maximum indicates the presence in the callogen associated with the composite. Thus, the results obtained confirm the existing opinion about the chemical interaction of this hydrophobizator with the functional groups of collagen.

Of decisive importance in maintaining the hygienic properties of natural leather is the nature of the distribution of hydrophobizing drugs in the structure of the dermis, which was examined using an ISN-2 scanning electron microscope [12-13]. As follows from Figures 2, the hydrophobization of the skin with the studied preparations leads either to a discrete distribution of the particles of the hydrophobizing agent on the skin fibers, or to the enveloping of the surface of the structural elements with a film of the preparation. In particular, the previously stated assumptions regarding the formation of a thin smooth PVEDOHS film on the surface of skin fibers during hydrophobization of an organosilicon liquid in the form of an emulsion were confirmed. On control samples of the skin awarded according to the standard technique, a dense spongy film is clearly visible. (fig. 5. V and VI option).

Taking into account that when processing a hydrophobizing composition based on polyvinyl dihydroxychlorosilane, a significant decrease in water permeability and wetness of the skin is achieved, it should be recognized that the existing opinion is correct that to obtain a sufficient hydrophobization effect, a uniform distribution of the hydrophobilizer is necessary on one third of the inner surface of the skin [14].

![Figure 5](image)

**Figure 5.** I-IV experimental variants, V-control, VI- untreated version of the skin.
4.1. Microscopic photographs of skin samples

As you know, the nature of the distribution of pores in effective diameters in combination with the total porosity and the chemical nature of the hydrophobizing composition have a significant effect on the hygienic properties of the skin, in particular on the vapor and air permeability, which is confirmed by the data given in table 1.

**Table 1.** Influence on the physical parameters of experimental and control skins depending on the type of hydrophobizators.

| Index                     | Leather samples |                           |                           |
|---------------------------|-----------------|-----------------------------|-----------------------------|
|                           | Experienced, processed control | Experienced, processed control |                           |
| Water repellent PVEDGHS Polyethylhydroxychlorosilane |                           |                           |                           |
| Air permeability, \( \text{sm}^3 / (\text{sm}^2 \times \text{h}) \) | 368             | 374                         | 387                         | 381                         |
| Water vapor permeability,\( \% \) | 77.1            | 77.9                        | 78.6                        | 78.1                        |

Note: Confidence intervals of the obtained results: porosity ± 2.2; air permeability ± 2.3; vapor permeability ± 1.6.* Determined by weight pycnometric method using kerosene.

From the data table 1 it follows that the porosity of the test leather samples and, consequently, their air permeability after hydrophobization decreases in comparison with the control samples. So, when processing leather, a hydrophobizing composition based on polyvinylethylid hydroxychlorosilane deposited on the surface of structural elements in the form of a film, air permeability decreases, and these samples are also characterized by lower porosity. With a discrete distribution of water repellents in the structure of the skin, the air permeability indicators change slightly.

The vapor permeability of experimental leather samples in some cases exceeds the control, which is explained by the alternation of hydrophilic and hydrophobic areas in micro-, meso- and macropores, which is one of the conditions for vapor permeability of fine-dispersed structures. [15-16].

In view of the fact that chrome leather is often used for upper shoes, which are often used in humid conditions, it seemed interesting to study the effects of the water repellents we obtained on the water resistance of chrome leather during cyclic moisturizing and drying. Skin samples moistened in various ways and dried to an air-dry state were subjected to cyclic wetting and drying. Humidification was carried out in water at a temperature of 30°C for 35 min, and drying under natural conditions for 48 h. The data obtained are presented in figure 6.

From the obtained results it is easy to notice that the samples, previously moistened with water, practically retain moisture absorption in 6-10 cycles of moistening. It is also seen that in the experimental versions, especially in the IV version, in all humidification cycles, the absolute humidity is less than in the control 1.5-2.0 times.

As a result of studies, it was found that the introduction into the composition of polymer-composite materials based on polyvinyl ethinyl dihydroxychlorosilane leads to an increase in the water-resistant properties of the leather of the shoe upper, by a factor of 1-2, compared with the control polyethylhydroxysiloxane.

The experiments also indicate that the samples, previously moistened with a control water repellent, have large values of the moisture absorption index. However, after 6-10 cycles, this indicator of skin samples, previously moistened with water, gradually stabilizes. This is obviously due to the fact that water in further processes in contact with the skin forms rather strong bonds with the structural elements of the dermis. Therefore, the wettability of chrome leather for the upper of the shoe increases, as a result
of which its water resistance of the shoe decreases.

![Figure 6](image)

Figure 6. The effect of the composition of water repellents on the sorption of moisture of chrome skin during cyclic wetting in water: I-IV - experimental and V - control components of water repellents.

This fact can be explained by the fact that after several treatments, simultaneously with the washing out of some of the hydrophilic components of the fatty emulsion, hydrophobizing drugs are fixed in the skin.

A decrease in the wetness of the skin treated with a composition based on PVEDHOCS occurs, obviously, as a result of additional polymerization of low molecular weight fractions of PVEDHOCS.

Thus, on the basis of the obtained results of the conducted studies, it can be concluded that for a more complete preservation of the hygienic properties of the skin in the process of hydrophobization, it is necessary to achieve a uniform distribution of water repellents in the skin structure.

In studies of the hygienic properties of waterproof leather for the top of shoes treated with water repellents, the sharpest decrease in water permeability under dynamic conditions is observed for a hydrophobized leather sample, which is associated with a sharp decrease in the water resistance of the skin under dynamic conditions by the destruction of the structure of hydrophobized surface layers under cyclic effects of deformation processes.

In studies, the hygienic properties of waterproof leather for upper shoes treated with water repellents most dramatically reduced water resistance under dynamic conditions is observed for a hydrophobized skin sample, which is associated with a sharp decrease in water resistance of the skin under dynamic conditions by the destruction of the structure of hydrophobized surface layers under cyclic effects of deformation processes [17-18].

In connection with the above, in order to determine the hygienic properties of waterproof leather for upper shoes trimmed on the basis of new water repellents after 24-hour logging, they were studied by known methods with subsequent statistical processing of the obtained data and determination of the arithmetic mean-square deviation, coefficient of variation and representativeness error for all the studied parameters of the samples with a probability of 0.95, the experimental error did not exceed 5-7%.

Table 2. Hygienic properties of experimental hydrophobized and control chrome tanned leather options.

| Test characteristics                              | Experienced I | II  | III | IV  | Control sample |
|--------------------------------------------------|--------------|-----|-----|-----|----------------|
| Water resistance in dynamic conditions, min       | 54           | 76  | 103 | 82  | 48             |
| Permeability under dynamic conditions, gr         | 0.63         | 0.57| 0.24| 0.36| 0.75           |
| Water permeability in static conditions (2 hours), sm³ | 3.06         | 2.64| 1.52| 2.12| 3.24           |
| Water permeability in static conditions (24 hours), sm³ | 5.18         | 4.57| 3.14| 3.46| 6.72           |
| Property                        | Value 1 | Value 2 | Value 3 | Value 4 | Value 5 | Value 6 |
|--------------------------------|---------|---------|---------|---------|---------|---------|
| Moisture absorption two hours, % | 81.7    | 74.3    | 52.3    | 62.4    | 86.4    |         |
| Wetness two hours, %           | 48.4    | 37.8    | 28.3    | 31.5    | 54.3    |         |
| Relative vapor permeability, %  | 0.21    | 0.23    | 0.28    | 0.25    | 0.19    |         |
| Absolute vapor permeability, (mg/sm² • h) • 10⁻⁴ | 4.1     | 5.8     | 7.8     | 6.3     | 3.2     |         |
| Steam capacity, %              | 13.1    | 15.8    | 19.6    | 17.3    | 12.4    |         |
| Hygroscopicity two hours, %    | 2.5     | 3.2     | 5.6     | 4.8     | 1.8     |         |

The analysis of the results was carried out in the following sequence: - the values of water permeability and water permeability were compared in the dynamic and static conditions of the control and treated samples, taking into account the positive effect of physical and hygienic and physical and mechanical properties. Otherwise, further tests were terminated. Subsequently, the properties of skin samples were studied before and after treatment with the selected technological methods of hydrophobization. So, the optimal combination of waterproof properties and properties that ensure the comfort of shoes was achieved. [19-20]

A significant effect was observed with hydrophobization III - an experimental version of chrome tanned leather (table 2).

Based on the above data, it can be noted that the test skin samples have the best hydrophobic properties. This is undoubtedly due to the water repellents introduced on the skin surface based on polyvinylethynylid hydroxychlorosilane, which, enveloping the fibrillar structures, form a film. At the same time, the number of pores increases in the inner surface of the skin.

5. Conclusions

For the first time, the possibility of using a new hydrophobizing composition in the process of finishing leather products has been established, which allows to increase the conformational transformations of the finished product and to streamline the supramolecular structure of the front surface of natural leather, leading to an increase in physical and mechanical properties and an increase in product quality.

By UV spectroscopy in collagen hydrolysates treated with hydrophobizing compositions based on PVEDHOHS, the results obtained confirm the existing opinion about the chemical interaction of this hydrophobizator with functional groups of collagen.

The decrease in the adsorption capacity of hydrophobized skin, due to new hydrophobized formulations, is explained by the additional action and nature of deposition on the facial surface of the skin in the form of separate globules in the microstructure of the skin.

Due to the specific composition introduced onto the facial surface of the skin, an increase in the number of small pores occurs, which will ultimately contribute to an increase in the rate of moisture condensation in them. Based on the above data, it can be noted that experimental skin samples have the best hydrophobizing properties.

This is undoubtedly due to polyvinyl ethinyl dihydroxychlorosilane-based water repellents introduced onto the skin surface, which form a film around the fibrillar structures. At the same time, the number of pores in the inner surface of the skin increases. Thus, it can be concluded that the use of polymers based on polyvinyl ethinyl dihydroxychlorosilane for the hydrophobization of chrome leather for upper shoes is feasible and effective.

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