ESTIMATION OF THE REGIMES OF ABLATION OF THE FABRIC OF KARAKUL FOR GLUTARALDEHYDE TANNING UNDER THE EXPOSURE OF A LASER ON YTTRIUM ALUMINUM GARNET

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ESTIMATION OF THE REGIMES OF ABLATION OF THE FABRIC OF KARAKUL FOR GLUTARALDEHYDE TANNING UNDER THE EXPOSURE OF A LASER ON YTTRIUM ALUMINUM GARNET

ABSTRACT. The article discusses the activation of the surface of karakul (astrakhan) leather tissue by laser exposure, changes in the surface morphology of karakul leather tissue during laser processing and subsequent glutaraldehyde tanning combined with chrome tanning of karakul leather. The morphology of the surface of the sample was investigated by the methods of optical and scanning electron microscopy and the elemental analysis of the skin tissue of karakul under the action of laser radiation from the front side was carried out. Dry tanning was carried out after laser exposure. For the first time, the morphology of the surface of the skin tissue of karakul was investigated using a laser generating in a two-pulse mode (pulses are separated by a time interval of 3 µs, pulse duration of 10 ns) with a wavelength of 1064 nm in a wide range of deposited energies, which lead, as to the mode of ablation of the surface of the skin tissue of karakul and to its perforation followed by glutaraldehyde tanning. The possibility of changing the consumer parameters of the skin tissue of karakul due to the dermis dissociation, conformational changes, which lead to a change in the structure, is shown. At energies more than 30 J, the skin is perforated with carbonization of the edges of the holes.

KEY WORDS: Karakul skins, glutaraldehyde, morphology, hydrothermal destruction, laser radiation

ESTIMAREA REGIMURILOR DE ABLAȚIE A PIELII DE KARAKUL PENTRU TĂBĂCIRE CU GLUTARALDEHIDĂ LA EXPUNERE SUB LASER CU IMPULSURI DE GRANAT DE YTRIU-ALUMINIU

REZUMAT: Articolul discută despre activarea suprafeței pielii de karakul (astrahan) prin expunerea la laser, modificările morfologiei suprafeței pielii de karakul în timpul prelucrării cu laser, precum și tăbăcirea ulterioară cu glutaraldehidă combinată cu tăbăcire în crom a pielii de karakul. S-a investigat morfologia suprafeței probei prin metodele de microscopie electronică optică și de scanare și s-a efectuat analiza elementară a pielii de karakul sub acțiunea radiației laser din partea frontală. S-a efectuat tăbăcirea uscată după expunerea la laser. Pentru prima dată, morfologia suprafeței pielii de karakul a fost investigată folosind un laser care funcționează în modul cu două impulsuri (impulsurile sunt separate la un interval de timp de 3 µs, durata impulsului de 10 ns) cu o lungime de undă de 1064 nm într-o gamă largă de energii depuse, care generează ablația suprafeței pielii de karakul și perforarea acestuia, urmate de tăbăcirea cu glutaraldehidă. Se prezintă posibilitatea de a modifica parametrii de consum al pielii de karakul din cauza disocierii dermei și modificărilor conformaționale care conduc la o schimbare a structurii. La energii mai mari de 30 J, pielea este perforată, având loc carbonizarea marginilor orificiilor.

CUVINTE CHEIE: piele de karakul, glutaraldehidă, morfologie, distrugere hidrotermală, radiații laser

L'ESTIMATION DES RÉGIMES D'ABLATION DE LA PEAU DE KARAKUL POUR LE TANNAGE AU GLUTARALDEHYDE LORS DE L'EXPOSITION AU LASER AU GRENAT D'YTTRIUM ET D'ALUMINIUM

RÉSUMÉ. L'article traite de l'activation de la surface du cuir de karakul (astrakan) par exposition au laser, des modifications de la morphologie de surface du cuir de karakul pendant le traitement au laser et du tannage ultérieur au glutaraldéhyde combiné au tannage au chrome du cuir de karakul. La morphologie de surface de l'échantillon a été étudiée par les méthodes de microscopie optique et électronique à balayage, et l'analyse élémentaire de la peau de karakul sous l'action du rayonnement laser de la face avant a été effectuée. Le tannage à sec a été réalisé après exposition au laser. Pour la première fois, la morphologie de surface de la peau de karakul a été étudiée à l'aide d'un laser fonctionnant en mode à deux impulsions (les impulsions sont séparées par un intervalle de temps de 3 µs, durée d'impulsion de 10 ns) avec une longueur d'onde de 1064 nm dans un large gamme d'énergies déposées, qui génèrent l'ablation de la surface de la peau de karakul et sa perforation, suivie d'un tannage au glutaraldéhyde. La possibilité de modifier les paramètres de consommation de la peau de karakul en raison de la dissociation du derme et des changements de conformation conduisant à un changement de structure est présentée. Aux énergies supérieures à 30 J, la peau est perforée, carbonisant les bords des trous.

MOTS CLÉS : peau de karakul, glutaraldéhyde, morphologie, destruction hydrothermale, rayonnement laser

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INTRODUCTION

Karakul skins are the main products of karakul sheep. The beauty, peculiar shape and originality of curls, their variety, noble shine and silkiness of the hairline, elegance of drawings brought fame to karakul skins. Karakul skins are in great demand among the population [1]. Therefore, great attention is paid to the quality of the karakul products.

Chemicals are used in the leather and fur industry for tanning skins from karakul fur, sheepskin, goat and other skins [2]. This is a method of tanning skins using a tanning composition based on the reaction products of polyoxymethylene with a secondary amine and alcohol and which are after the reaction in the form of tertiary amino groups and ether groups [3].

Laser technologies are increasingly being introduced into the production of products from karakul leather fabric. Laser radiation has coherence, monochromaticity, collimation, which makes it unique. The interaction of laser radiation with the skin tissue of karakul is based on its physical properties [4-6].

The main physical parameters that determine the effect on natural skin are the generated wavelength and power density [4, 7]. It is also important to take into account the inhomogeneity of the spectral absorption of the karakul skin tissue, since hemoglobin has many absorption peaks, and the absorption of melanin gradually decreases as the wavelength of light increases. To activate chemical reactions on the surface of the skin tissue of karakul or to remove defects, ablation of the area of the affected skin tissue of karakul, including the epidermis, is carried out. Laser ablation is understood as a complex of processes that lead to an explosive ejection of a substance from the zone of exposure to laser radiation. Of interest are the modes in which the removal of the substance from the zone of action occurs quickly enough that the areas of the karakul skin tissue surrounding the laser crater do not have time to heat up due to the transfer of heat.

The aim of this work is to study the morphology of the surface of natural leather during laser ablation to establish the conditions for perforation of the leather tissue of karakul; glutaraldehyde tanning was combined with chrome tanning in the double pulse mode.

EXPERIMENTAL PART

Objects of Study

Karakul (Uzbekistan. Karakul – diminutive of "karakul, sheep of the Karakul breed"; from Uzbek. Karakul "Black Lake", after the name of the city and area in Uzbekistan) – fur made from the skins of premature lambs (miscarriages in the last period of pregnancy) or fruits (extracted from the womb of slaughtered queens) of karakul sheep, as well as products made from this fur [8].

Karakul literally translates from Turkic, black as ash (karakul) – skin with fur, removed from lambs of the Karakul breed on 1-3 days after birth, when their wool is characterized by thick, elastic, silky hair, forming curls of various shapes and sizes [8].

Glutaraldehyde (glutaraldehyde, pentane dial) is an organic compound, an aldehyde with the chemical formula $C_5H_8O_2$. Transparent and colorless liquid, easily soluble in water, irritating to eyes and lungs. It is used as a tanning agent in the production of leather, and is used in the textile industry and microscopy [9].

Methodology and Research

Laser Radiation

In this work, we used laser processing in the mode of double pulses of a sample of karakul leather tissue. We used an LS-2134D yttrium aluminum garnet laser (LOTIS, Belarus) with a wavelength of 1064 nm, generating in a two-pulse mode (the pulses are separated by a time interval of 3 μs, the pulse duration is 10 ns). The sample was treated with laser radiation in the energy range of 1–30 J at exposure times of 1–30 s [10].

SEM Research and Elemental Analysis

The study of the surface morphology of the leather was carried out using a MIRA-3 scanning electron microscope (Czech Republic) with a system of micro analyzers from Oxford Instruments (Great Britain). The device allows you to simultaneously study the surface morphology of the material, determine the distribution of chemical elements of the sample, and also obtain an image of the object in a wide range of magnifications. The thickness of the leather sample is ~500 µm [11].

Magnetic Resonance

Magnetic resonance studies were carried out on a specialized small-sized EPR analyzer Minsk 22 at room temperature. The working wavelength is 3 cm. The maximum value of the magnetic field induction is 450 mT. The modulation frequency of the magnetic field is 30 kHz. To calibrate the signal intensity of the objects of study, we used a sample from a ruby single crystal (Al_2O_3: Cr^{3+}). The optimal parameters for recording the working magnetic resonance spectra were chosen in the range of g-factors from 1.5–4.0. During measurements, an additional control of the stability of the spectrometer was carried out by measuring the calibration material of divalent manganese ($MgO{\cdot}Mn^{2+}$) [10].

RESULTS AND DISCUSSION

In this work, we used laser processing of leather tissue in the dual pulse mode. An LS-2134D yttrium aluminum garnet laser (LOTIS, Belarus) with a wavelength of 1064 nm was used, which generated in a two-pulse mode (pulses were separated by a time interval of 3 µs, pulse duration 10 ns) [11]. The energy input was determined by the exposure time and ranged from 1 to 30 J. During the research, we used unpainted waste of karakul leather fabric (made in Uzbekistan). Samples of tanning fabric karakul semi-finished product from the front side were treated with laser radiation. After pickling or fermentation, the skin tissue of the skin acquires strength, ductility and other useful qualities necessary in the manufacture of fur products. However, its strength can be compromised when wearing a finished fur product. Under the influence of moisture (rain or snow), peeling, swelling of the leather fabric of karakul fur can occur, and subsequently such fur products wrinkle and warp. To avoid these undesirable phenomena, tanning is carried out.

The purpose of tanning is to consolidate the properties obtained during pickling, to make the skin resistant to unfavorable factors – heat, moisture, chemicals and enzymes. Tanning agents of inorganic origin include compounds of aluminum, iron, titanium, zirconium and others, and organic ones – tannins, amino resins, aldehydes, highly unsaturated fats, etc. [12].

Tanning is a complex process that begins with the diffusion of tanning compounds into the structure of collagen protein, with which it then interacts, forming strong chemical compounds in the leather tissue of karakul fur. Under the influence of tanning compounds, collagen acquires new properties: its heat resistance, characterized by the welding temperature, increases, strength increases, porosity of the karakul leather tissue decreases, swelling disappears, and chemical resistance increases. When dressing skins (mostly sheepskins), glutaraldehyde tanning can be used.

In any case, it must be remembered that aldehydes are capable of dyeing fur white. Therefore, it is recommended to tan skins with white fur with aldehyde. Samples of tannery karakul semi-finished product were placed in a solution of sodium chloride (NaCl) with the addition of acetic acid (treatment for 2 hours), then glutaraldehyde was introduced (treatment for 4 hours), then baking soda was added (treatment for 1 hour).

Then the samples of the leather fabric of karakul fur were squeezed out and left to lie down, dried and kneaded. All processes were carried out at a temperature of 30°C. Leather treatment with glutaraldehyde, in addition to softness and elasticity, is characterized by a higher resistance to sweat and moisture in comparison with chrome tanning [13-15]. Glutaraldehyde tanning has been combined with chrome tanning.

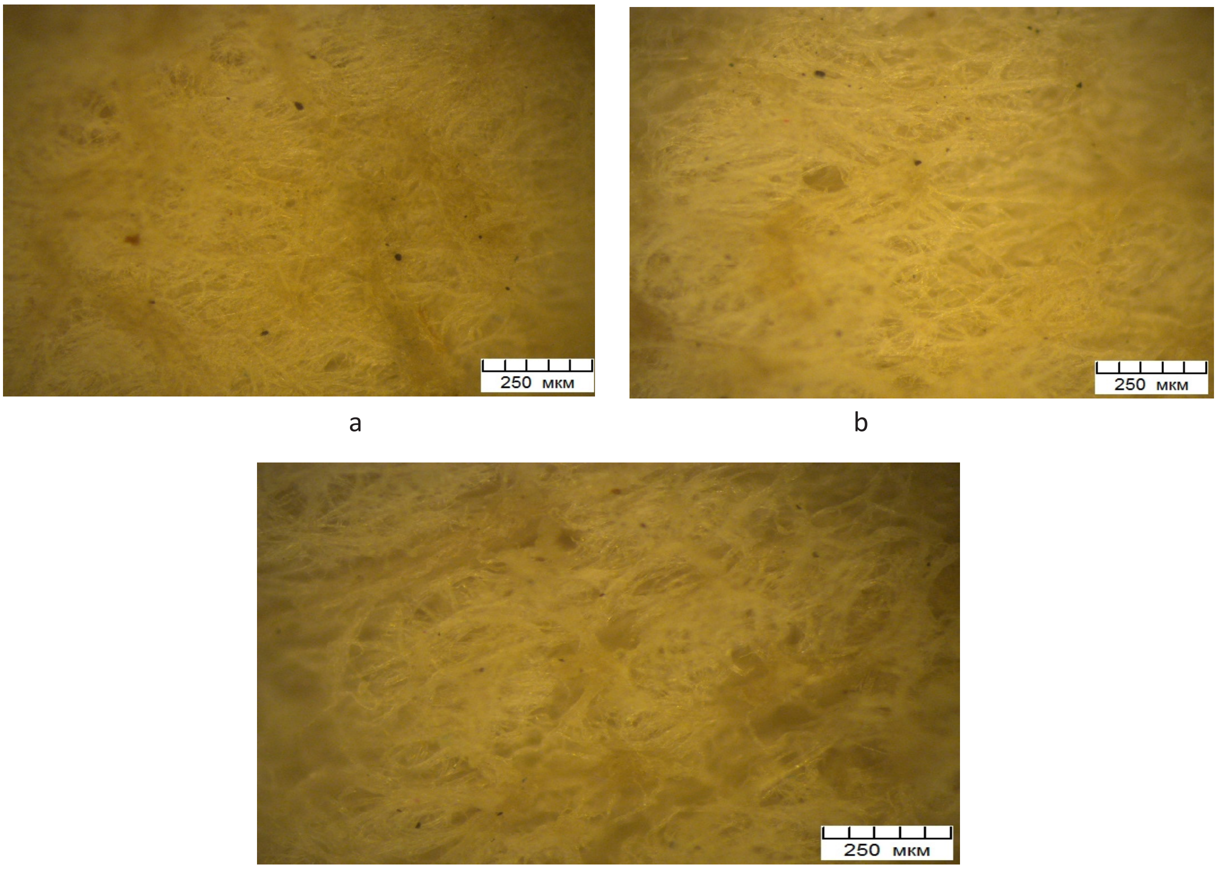
Modern metallographic microscopes using various methods of optical contrasting make it possible to study the structures of non-metallic materials. In this work, an inverted metallographic microscope MI-1 was used to study changes in the surface morphology of the skin tissue of karakul. The analysis of the skin surface was carried out at 100x magnification using dark field illumination.

The study of the chemical composition of karakul leather tissue was carried out using a scanning electron microscope MIRA-3 (Czech Republic) with a system of micro analyzers from Oxford Instruments (Great Britain). The device allows you to simultaneously investigate the morphology of the material surface, determine the distribution of chemical elements of the sample under study, and obtain an image of the object in a wide range of magnifications.

In accordance with [4], under the influence of the first laser pulse, the substance evaporates, and a region with an increased temperature and a reduced density of air particles is formed in the near-surface layer, which leads to a more complete use of the energy of the second pulse for laser ablation [4]. It is known that when exposed to a series of nanosecond pulses, the main mechanism for removing a substance is thermo-mechanical ablation, which leads to the removal of the surface layer.

When exposed to IR laser radiation, energy is absorbed on the surface of the tanning fabric of the karakul semi-finished product. It is known that the nature of light erosion is largely determined by the characteristics of the material itself: optical, thermo-physical properties, structural in homogeneities, etc.

Figure 1 shows the surface of the karakul skin tissue that was not exposed to laser action and was exposed to laser action with different input energies.



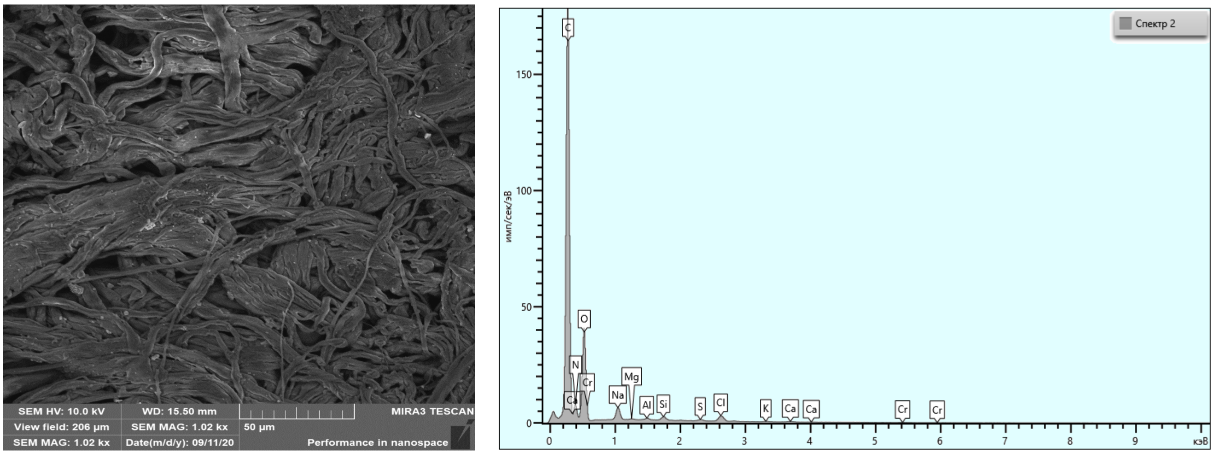
a b

c

Figure 1. Morphology of the surface of the front side of the fabric of karakul before and after laser exposure: a) without exposure, b) after exposure (input energy 1 J, exposure time 1 s), c) after exposure (input energy 5 J, exposure time 5 s)

It follows from Figure 1 that with an increase in the energy deposited into the sample, the structure loosens (the fibers move apart) and the pore size increases. So, the size of the pores varies from 30 to 50 microns (Figure 1b) and from 50 to 125 microns (Figure 1c).

Figure 2 shows the structure and elemental composition of karakul leather fabric after chrome and glutaraldehyde tanning.



a b

Figure 2. Morphology of the surface of the face of the fabric of karakul after laser exposure: a) after exposure (input energy 5J, exposure time 5s)

Individual collagen fibers with a thickness of 1-2 microns are clearly visible, the joints of these collagen fibers form bundles of fibers 10-50 microns thick, intertwining in different directions to form a complex dermis tissue.

Figure 3 shows the morphology of the karakul skin tissue after laser exposure, during which the karakul skin tissue is perforated. Laser perforation is performed in the production of clothing, handbags and other products, mainly for decorative processing.

However, due to the porosity of the karakul leather tissue, there are also problematic issues, in particular, the combustion process when exposed to a laser beam, as well as the remnants of material inside the hole due to the fuzzy study of the hole in these modes. Therefore, it is necessary to investigate the modes of laser processing of karakul leather tissue in the process of its perforation.

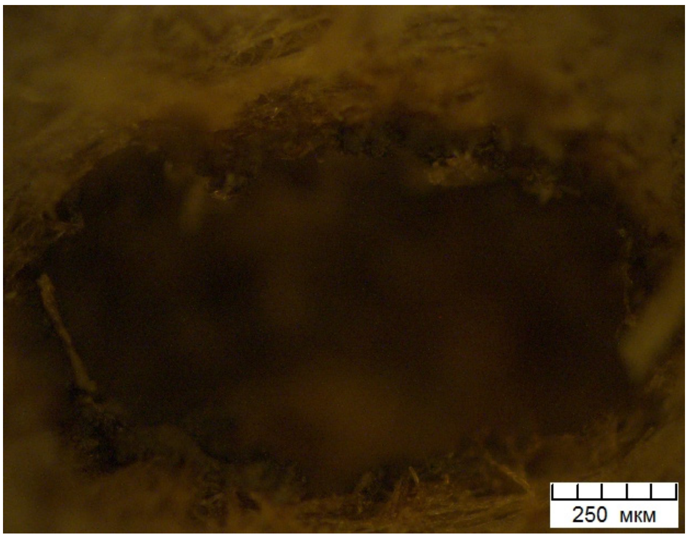
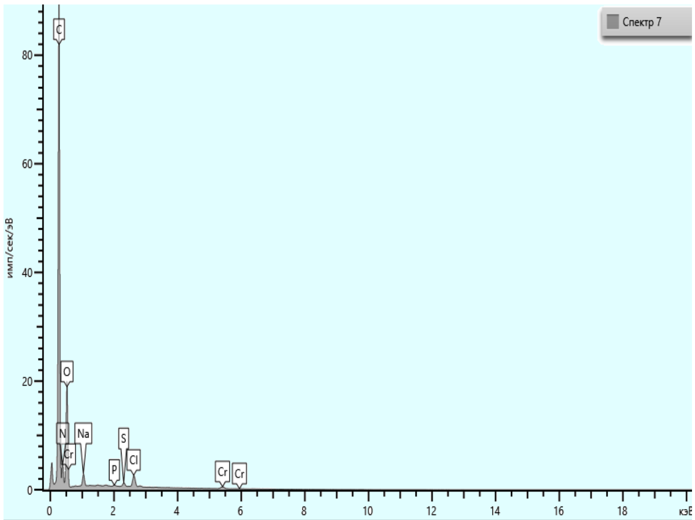


Figure 3. Morphology of the surface of the face of the fabric of karakul after laser exposure: after exposure (input energy 30 J, exposure time 30 s)

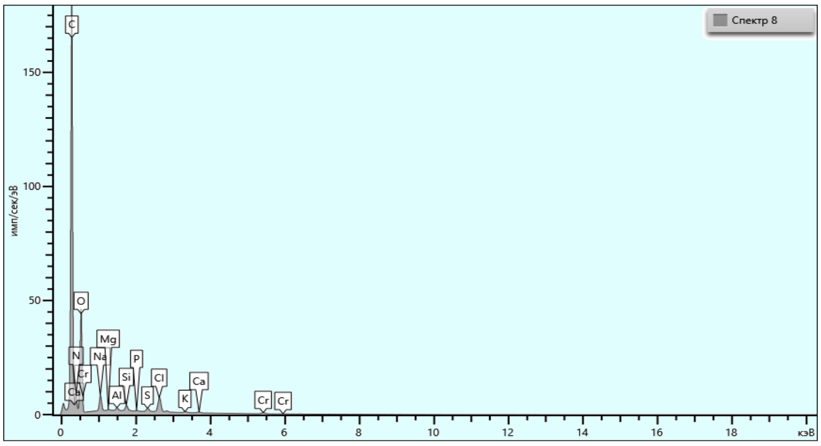
From Figure 3 it follows that at energies more than 30 J, perforation of the karakul leather tissue occurs and carbonization is observed at the edge of the hole, the size of the perforated hole reaches approximately 1100 microns.

Figure 4 shows the surface morphology and elemental composition of the karakul leather tissue (scanning microscopy) in the mode of its perforation.

a



b



c

Figure 4. Surface morphology and elemental composition after laser exposure: a) in the perforation zone (input energy 30J, exposure time 30 s), b) at the periphery of the exposure zone, c) spectra of the elemental composition of the peripheral crater

Table 1: Elemental analysis results

Result type	Spectrum label													
	C	N	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Cr	Total
Spectrum 7, wt%	56.74	15.01	25.21	0.88	-	-	-	0.09	0.28	1.06	-	-	0.73	100.00
Spectrum 8, wt%	55.73	13.29	26.64	1.25	0.16	0.25	0.34	0.15	0.27	1.46	0.13	0.15	0.45	100.00

As can be seen from Figure 4, in the perforation zone, there is a sharp change in the structure of the karakul leather tissue. The process of carbonization takes place, water is removed, and the pores increase to ~100 µm. There is also a change in the elemental composition, so in the perforation zone there is an increase in carbon and a change in the concentration of other elements, which is associated with the processes of carbonization of the leather tissue of karakul.

Thus, depending on the energy input, both the process of ablation of the karakul skin tissue and the process of its carbonization are observed.

At the next stage of research, the tanning action of glutaraldehyde, which is formed directly in the structure of the dermis, was studied. The polycondensation process was carried out due to acid tanning chromium compounds. The concentration of glutaraldehyde was 3.0 g/l, chromium compounds (calculated as Cr_2O_3) 1.0 g/l, CK = 8.0, temperature 35°C. The tanning effect was determined by the welding temperature of comparable samples of karakul leather by treatment with glutaraldehyde and formaldehyde (Figure 5).

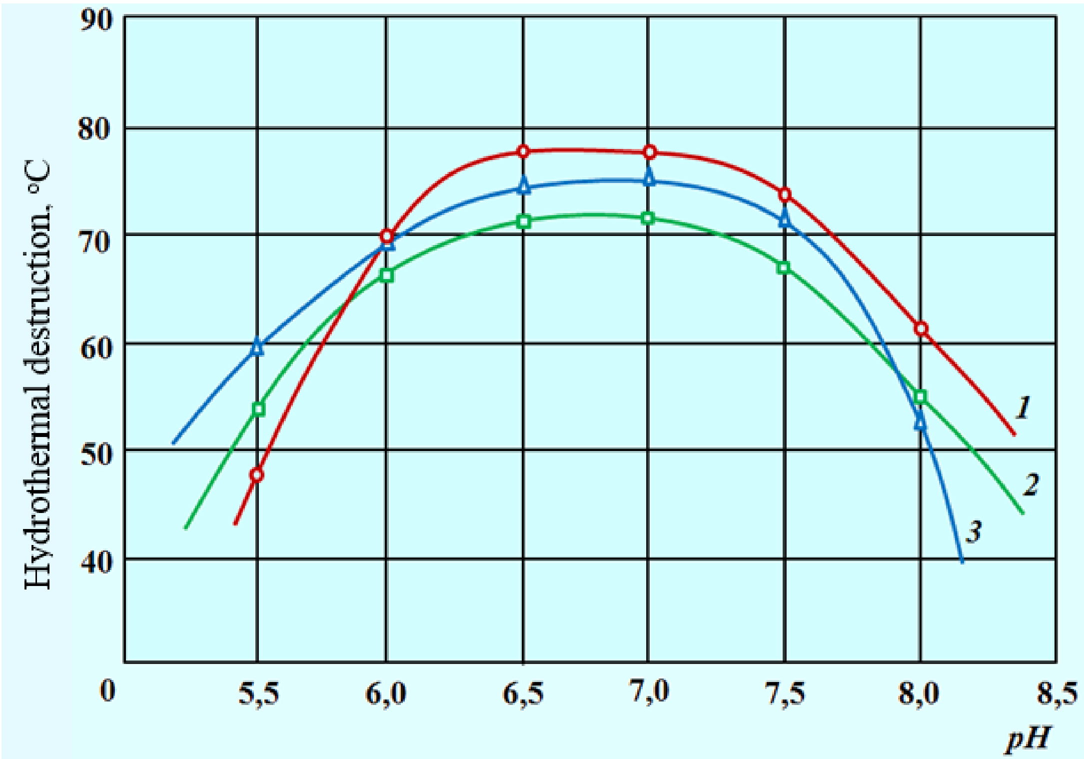


Figure 5. Dependence of hydrothermal degradation in the pH environment after tanning fabric of karakul semi-finished product

Treated variants: 1 - glutaraldehyde, 2 - formaldehyde and 3 - chromium compounds

As can be seen from Figure 5, the processing of karakul leather with glutaraldehyde gives the semi-finished product a higher welding temperature, which indicates a stronger tanning ability of glutaraldehyde. The reason for this is the stronger binding of the molecular chains of collagen by glutaraldehyde, which is formed in the structure of the dermis under the conditions of tanning, than when tanning with formaldehyde and chromium.

The results of the study of the physicochemical properties of karakul leather fabric for tanning with glutaraldehyde are presented in Table 2.

Table 2: Physicochemical properties of karakul leather fabric for glutaraldehyde tanning

№	Indicators	Control	Experienced	State standard 10151-2014
1	Free formaldehyde content, μg / g	33	18	no more than 300
2	Content of water washable chromium (VI), mg / kg	2.8	1.2	no more than 3.0
3	Temperature welding leather tissue, °C	73	78	at least 50
4	pH water hoods leather tissue	3.9	4.1	at least 3.5
5	Sustainability coloration hair cover to dry friction, points	4	5	at least 4
6	Color fastness of leather fabric to dry friction, points	4	4	at least 3

The glutaraldehyde tanned karakul leather fabric has a light brown color, is distinguished by its softness, high color fastness of the hairline and leather fabric to dry friction.

CONCLUSIONS

For the first time, the morphology of the surface of the skin tissue of karakul was investigated using a laser generating in a two-pulse mode (pulses are separated by a time interval of 3 μs, a pulse duration of 10 ns) with a wavelength of 1064 nm in a wide range of deposited energies, which lead, as a mode of ablation of the skin surface, followed by glutaraldehyde tanning, and to its perforation with an increase in the input energy. The modes of laser processing have been determined, which make it possible to switch from the ablation mode (removal of small defects and leveling the skin surface for further processing), and to the perforation mode (obtaining holes for cosmetic purposes).

The possibility of changing the consumer parameters of the skin tissue of karakul due to the dermis dissociation, conformational changes, which lead to a change in the structure, is shown. At energies more than 30J, perforation of the karakul leather tissue occurs with carbonization of the edges of the holes.

A decrease in tanning ability is clearly expressed in formaldehyde solutions, this provides a strong bond of dermal elements with glutaraldehyde. The leather fabric of karakul fur is more resistant to leather fabric to dry friction than leather fabric of karakul fur with formaldehyde and chrome tanning.

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