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EVALUATION OF THE ABLATION MODES OF THE GUARD'S LEATHER TISSUE FOR TANNING GUTARIC ALDEHYDE UNDER THE ACTION OF A LASER

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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 was 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.

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 smushka products.

Chemical processing of skins, namely for tanning skins, and is intended for use 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.

MATERIALS

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 suagnosti) 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].

METHODS

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].

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 pickling, 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 - tannies, 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 morphology of the karakul skin tissue after laser exposure, during which the karakul skin tissue is perforated. Laser perforation is carried out in the production of clothing, handbags and other products, mainly for decorative processing.

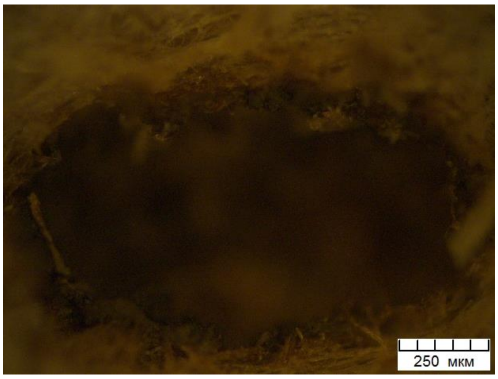
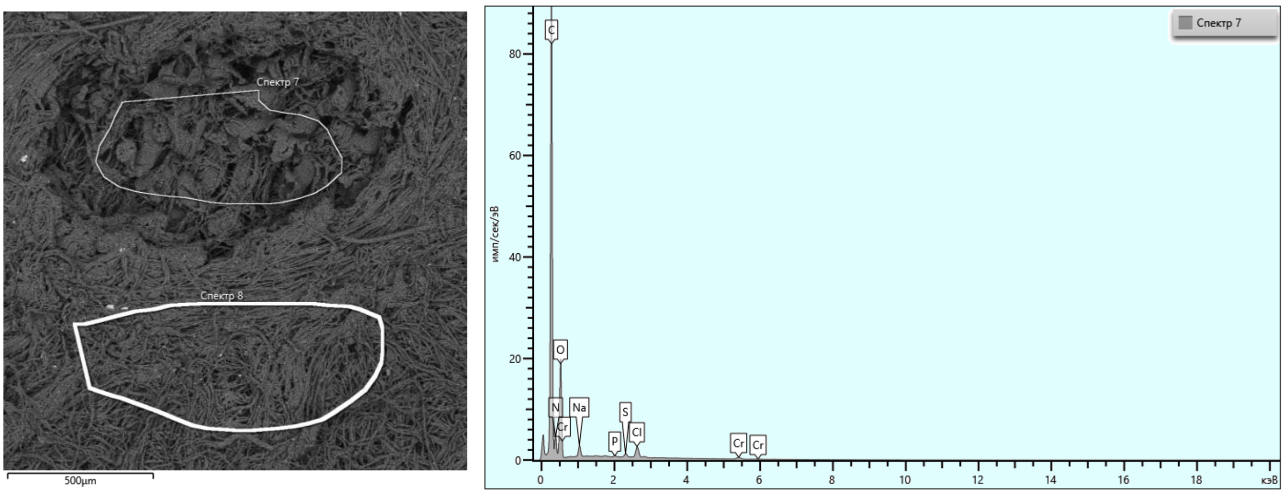


Fig 1. Morphology of the surface of the face of the fabric of karakul after laser exposure: after exposure (input energy 30 J, exposure time 30 s).

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 elaboration 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 1 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 2 shows the surface morphology and elemental composition of the karakul leather tissue (scanning microscopy) in the mode of its perforation.



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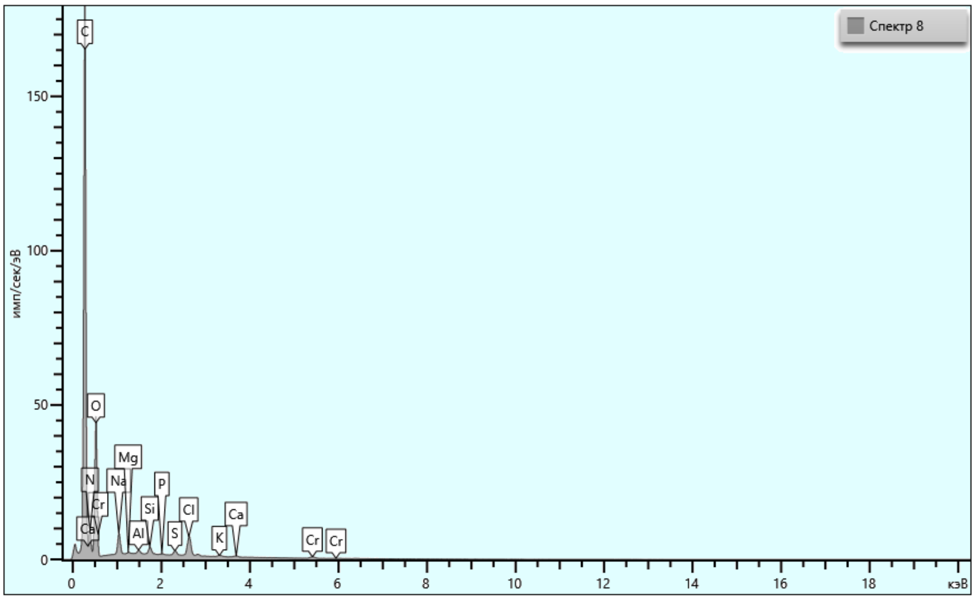

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Fig 2. Surface morphology and elemental composition after laser exposure: a) in the perforation zone (input energy 30J, exposure time 30 s), b) at the periphery of the exposure zone..

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.

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 astrakhan 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.

The results of the study of the physico-chemical properties of astrakhan leather fabric for tanning gulutaraldehyde are presented in table. 2.

table. 2

Physico-chemical properties of astrakhan leather fabric for glutaraldehyde tanning

№	Indicators	Tests	Experienced	GOST 10151-2014
1	Content of free formaldehyde, μg/g	33	18	no more than 300
2	Content of water-leached chromium (VI), mg/kg	2,8	1,2	no more than 3,0
3	Leather fabric welding temperature, °C	73	78	at least 50
4	pH of leather extract water	3,9	4,1	at least 3,5
5	Hair color fastness to dry friction, points	4	5	at least 4
6	Color fastness of leather fabric to dry friction, points	4	4	at least 3

A decrease in tanning ability is clearly expressed in formaldehyde solutions, this ensures a strong connection of the elements of the dermis with glutaraldehyde. Astrakhan leather fabric is more resistant to dry friction than astrakhan leather fabric with formaldehyde and chrome tanning.

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 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, and to the perforation mode. 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.

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