International Journal of Recent Technology and Engineering (IJRTE)
ISSN: 2277-3878 (Online), Volume-8 Issue-6, March 2020

Researches of Morphological Structure, Element Composition And Natural Leather Adsorption By Exposure to Laser Radiation

Kodirov T.J., Markevich M.I., Malyshko A.N., Zhuravleva V.I., Sodikov N.A.

***Abstract: Annotation.** Scanning electron microscopy studied microphotographs of a longitudinal section of a bundle of collagen fibrils of the reticular layer of a leather tanning product of chromium tanning from cattle hides. The distribution of chrome tanning agent over the leather thickness in the initial sample was studied. The effect of laser exposure on the microstructure of the leather is investigated. It was found that laser irradiation (input energy 40 J, exposure time 40 sec) leads to a slight increase in pore size and loosening of its structure. It was established that in the process of laser radiation, collagen fiber bundles first swell with their own capillary moisture, then they are separated, i.e. they break up into individual microfibrils. An elemental analysis of the distribution of chromium over the leather cross section showed that the chromium compound penetrates the entire thickness of the leather, however, the chromium distribution varies significantly with thickness. The effect of laser radiation on the process of sorption-desorption of water by the leather is revealed. From the data obtained it was found that laser leather training changes its ability to adsorb water vapor and desorb moisture from the environment.*

***Keywords:** laser radiation, fibril, chrome tanned leather, microstructure leather, two-pulse processing mode, sorption, morphological structure, collagen fiber, separation, cross section, leather pore desorption, relative humidity.*

I. INTRODUCTION

Natural leather products are in great demand and are widely used, despite the relatively high level of manufacture of similar products from synthetic and artificial fibers. This trend is associated with high hygroscopicity, wear resistance, capillarity, biocompatibility and individuality of the pattern of genuine leather.

Manuscript received on February 10, 2020.
Revised Manuscript received on February 20, 2020.
Manuscript published on March 30, 2020.
* Correspondence Author
Kodirov T.J*., Tashkent Institute of Textile and Light Industry, 100100, st. Shohzhahon-5, Tashkent, Republic of Uzbekistan
Markevich M.I., Physical and Technical Institute of the NAS of Belarus, ul. Kuprevich, 10, **220141**, Minsk, Belarus
Malyshko A.N., Military Academy of the Republic of Belarus, Independence Ave. 220, 2200057, Minsk, Belarus
Zhuravleva V.I., Military Academy of the Republic of Belarus, Independence Ave. 220, 2200057, Minsk, Belarus
Sodikov N.A., Tashkent Institute of Textile and Light Industry, 100100, st. Shohzhahon-5, Tashkent, Republic of Uzbekistan

One of the features of genuine leather is its porous structure. Recently, for the physical modification of porous structures (natural leathers), a plasma treatment method has been proposed in the high-frequency discharge of low pressure [1,2]. The technology of leather and fur materials [3] is presented, which allows to increase the percentage of use of

low-grade raw materials and the grade of the semi-finished product by regulating the technological properties of the dermis and hairline at all stages of dressing due to the use of high-frequency plasma processing. As a parameter characterizing the hydrophilic properties of the material, two-hour wetting in distilled water was chosen. In the initial state, the wettability of wet-salted raw materials from cattle leathers is 20%, and the raw materials from sheep leathers of a fresh-dried canning method are 83%. The greatest wettability of raw material samples is observed under the plasma treatment regime $\tau = 3$ min, P = 13.3 Pa.

The results of studies of possible ways to intensify technological processes using electromagnetic waves of the high-frequency and microwave ranges are presented [4].

Despite the great progress in understanding the physical processes that occur in the technology of leather dressing, the processes under laser exposure to the leather (changes in the morphology of the surface of the leather in a two-pulse treatment mode) remain practically unstudied.

The relevance of studying these issues is determined both by the needs of basic research, and by numerous important practical applications.

purpose of work - to establish the features of laser modification in the dual pulse mode on the surface morphology of natural leather.

The advantages of laser processing methods for genuine leather materials that reduce the cost of the process and improve product quality:

- high speed of the process;
- lack of deformation of the material outside the processing zone;
- processing of the minimum surface area (approximately 10–20 μm);
- lack of material distortion due to non-contact processing;
- precise cutting of thin contours;
- sterility of exposure.

II. EXPERIMENTAL PART

Objects of study

Half-leather. Half-leather - leathers of young cattle (telly and gobies) weighing more than 10-13 kg in pairs, which corresponds to animals

weighing from 150 to 200 kg. Such leathers are obtained from animals aged 1.0-1.5 years, and from heavy thoroughbred cattle with good feeding - at the age of 8-10 months. The leathers of winter-spring slaughter are distinguished by a large overgrowth, coarse

dull hair with a small amount of fluff. On the leathers of the half-leather, there is a pronounced escape rate, but much less than in older animals. The thickness of the leather in the back varies from 2.5-3.0 mm. The bundles of collagen fibers are thin, and their plexus is quite dense.

Mereya leathers, made from the leather of a half-leather, are rougher than the outgrowth. Half-leather leathers obtained from gobies, especially from low-fat animals, are brooches. Half-leather is mainly processed into chrome, yuft and technical leather.

Chrome tanned leather. For the study, we used colored chrome leather wastes with the following physicochemical parameters. B %: humidity-52,4; total ash-4,8; fatty substances - 3,2; dermal substance - 76,83; chromium oxide - 5,2 and hydrothermal destruction 92,0 °C

Methodology and research tools

Laser radiation. In this work, we used laser processing in the regime of double pulses of a sample of genuine leather. LS-2134D ittrium-aluminum grenade 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).

SEM research and elemental analysis. The study of the surface morphology of the leather was performed using a MIRA-3 scanning electron microscope (Czech) with a system of microanalyzers from Oxford Instruments (Great Britain). The device allows you to simultaneously study the morphology of the surface of the material, determine the distribution of chemical elements of the test sample, and also obtain an image of the object in a wide range of magnifications. The thickness of the leather sample is ~ 500 μm [6].

Sorption of water with leather. Sorption research were carried out on a Mc Ban vacuum balance with a quartz spring in the range of relative humidity from 0% to 100%. Then, using the BET equation [7,8].

III. RESULTS RESEARCH AND DISCUSSION

Research of the morphological structure of chrome tanned leather by laser radiation

The theoretically substantiated technology [9], combining plasma treatment with subsequent tanning with monomeric difunctional urethane, apparently allows to exclude the use of chromium compounds, implemented on the example of tanning fur sheepleather.

It has been shown [10] that the plasma effect in the presence of polymers on the nanostructure of leather and fur materials allows one to obtain a semi-finished product with controlled technological and operational properties: in fur semi-finished products, the temperature of destruction increases by 3-6 ° C, the tensile strength by 10-13% ,

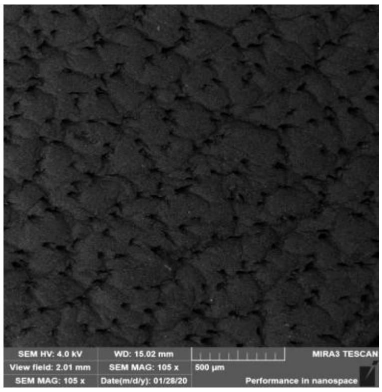


Fig. 1. Morphology of the leather surface before laser exposure.

also, developed [11] the scientific foundations and technologies for producing leather and fur materials to increase the percentage of use of low-grade raw materials and the grade of the semi-finished product by regulating the technological their properties of the dermis and hairline at all stages of production due to the use of high-frequency plasma treatment.

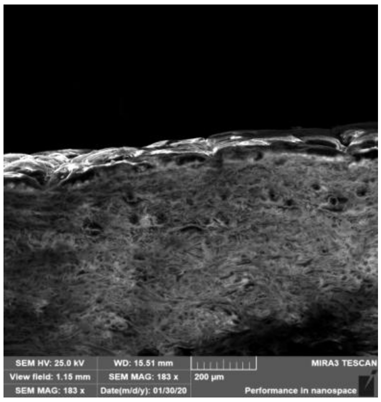
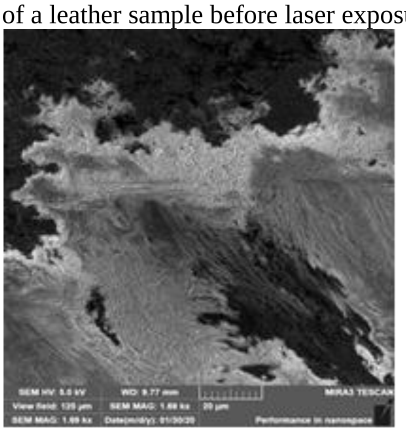
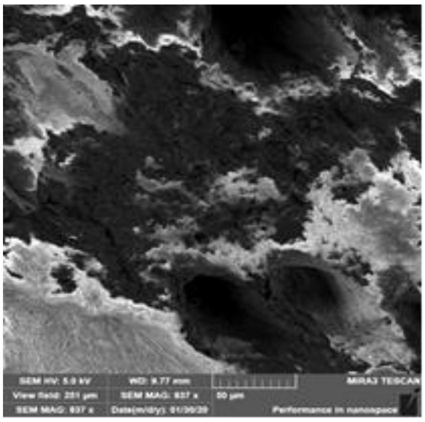


Fig. 2. Morphology of the surface of the cross section of the leather before laser exposure.

In fig. 1 clearly visible pores, the size of which varies from 40 to 60 microns. Figure 2 shows the structure of the cross section of a leather sample before laser exposure



A)



B)

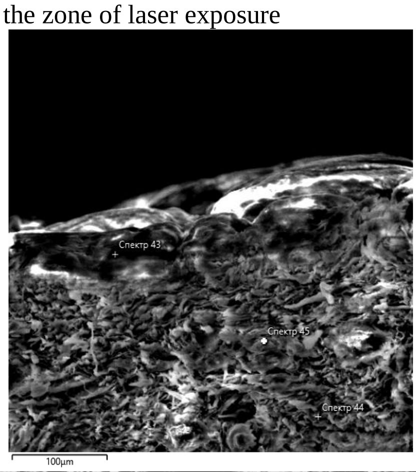
As can be seen from fig. 2, the leather structure is not uniform in thickness. So at a thickness of about 60 μm, a densified surface layer is observed, below which collagen fibers are less densified.

The centers of intermolecular interaction in the structure of collagen are various hydrophilic groups of its

structure: peptide, carboxyl, hydroxyl, as well as basic groups.

In the aquatic environment, most of them are hydrated. Their ability to form intermolecular bonds is used to interact with water.

In fig. III, shows the structure of the facial surface of the leather in the zone of laser exposure



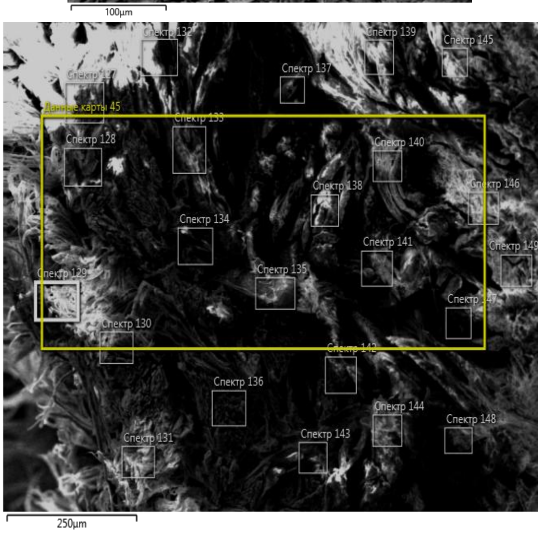


Fig. 4. Sections of the leather dermis selected for elemental analysis of the distribution of chromium over the cross section of the leather sample.

The surface structure of the leather after laser irradiation with an input energy of 40 J and an exposure time of 40 sec at various magnifications (Fig. 3. a, b).

As follows from Figure 3, the structure of collagen fibers is loosened (Fig. 3 a) and an increase in pore size has occurred.

Also, the distribution of tanning agent in the morphological structure of the leather is of interest.

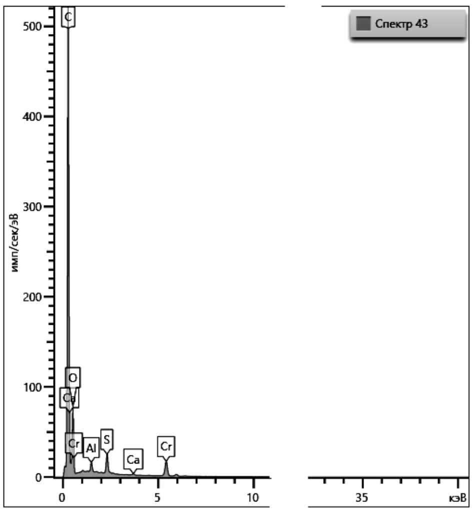
It was established [13] that high-frequency plasma processing of leather raw materials in the technology for the production of Wet-Blu chrome tanning semi-finished products leads to morphological changes in the

supramolecular collagen structures, which are manifested in the enlargement and separation of fibrils and fibers in raw materials, and the separation of fibers and bundles in glue and in the semi-finished product. Processing of raw leather from sheepleather leathers in the mode Wp = 1,3 kW, P = 13,3 Pa, GAr = 0.04 g / s, t = 5 min. leads to an increase in assertiveness in it by 118%. The initial thermophysical parameters of the structural stability of the gilded split-off trimmings (the temperature of the onset of hydrothermal contraction, the temperature of welding, - fluidity, and the phase transition energy) are characterized.

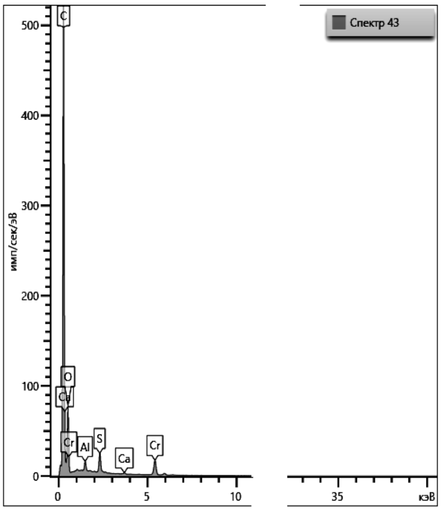
Studied [14], tannins catalyzed by the enzyme and covalent crosslinking based on aldehydes, electrostatic and hydrophobic interactions. Factors contributing to the stabilization mechanism include covalent crosslinking, electrostatic interactions, hydrophobic interactions, hydrogen bonds, and water activity. A collagen model has been developed to study the interactions of collagen with a tannin, especially in the less dense microfibril fracture region.

In this regard, a study was made of the distribution of chrome tanning agent over the thickness of the leather

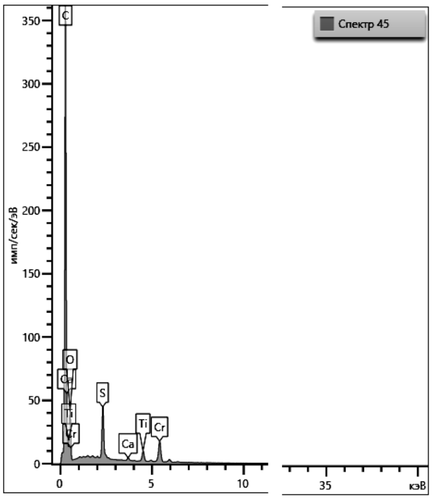
in the initial sample (Fig. IV). Since, according to the technology of leather production, the salt of basic chromium sulfate (Cr_2O_3) is introduced as an obligatory element at the stage of its tanning as a cross - linking agent for leather collagen.



A



Б



В

Fig. 5. Elemental analysis of the distribution of elemental chromium over the cross section of a leather sample.

Analysis of the distribution of chromium over the leather section shows that the chromium compound penetrates the entire thickness of the leather, however, the distribution of chromium varies significantly with thickness.

So on the front surface of the leather (spectrum 43), the chromium content is 1.42 wt.%, Which is possibly associated with subsequent technological stages of its processing. The maximum chromium content at point 44 (spectrum 44) at a depth of approximately 230 microns (8.11 wt.%). At point 45, the chromium content is greater than at point 43 and amounts to 1.98 wt.% (Fig. 5).

Moreover, in the process of laser radiation, this water is split off. In exchange, due to the same affinity forces, intermolecular hydrogen bonds are formed between the elements of the protein structure.

This occurs between molecular chains in the thickness of structural elements, as well as on the surface of the facial layer of the leather (Fig. 3). In this latter case, the formation of intermolecular bonds can be considered adhesion.

In the process of interaction with dermis, various tanning agents react with the same hydrophilic centers of the collagen structure as water. Unlike water, tanning particles are not removed during the drying process.

Therefore, after laser irradiation of the leather semi-finished product, the intermolecular interaction forces necessary for the formation of adhesion remain saturated in this case, and no bonding occurs.

Thus, it can be considered established that the formation of the volume of the leather semi-finished product, in addition to reducing its deformability, is also due to the fact that the surfaces of the interstitial pores penetrating it have lost the ability to skeletal.

The effect of laser radiation on the process of sorption-desorption of water by the leather

The interaction of leather with moisture is usually characterized by a complex of chemical and physico-chemical processes. Therefore, using simpler model systems, it is advisable to consider and transfer the found patterns into real porous materials [15].

In this regard, from the beginning it is important to consider methods of studying the structure of porous materials and explain the basic concepts that characterize their most important properties, primarily porosity [16]. Effective porosity is expressed as the ratio of the volume of communicating pores to the total volume of the porous body. However, in the microstructure of capillary-porous materials, which include the leather, there are dead-end or closed pores. Closed, porosity is characterized by both absolute and effective porosity.

Clarification of the problem of the effect of hydrophobization on the sorption-desorption of water by the leather and its porosity is of interest both from the point of view of the hygienic properties of the leather, and for carrying out some technological processes to determine the durability of shoes [17,18].

Therefore, studies have determined the effects of laser radiation on the processes of sorption-desorption of water by the leathers, both the control (non-emitted) and experimental leather samples.

The amount of moisture adsorbed by experimental leather samples in an atmosphere with different relative humidity is presented in table. (data on average results)

Table-1

The amount of moisture sorher by leather sampler in an atmosphere with different relative humidity

Relative humidities, in %	Options	
	Control without laser radiation	Experienced with laser radiation
	Sorption, in%. Moisture (per 100 g of dry leather) at relative humidity φ.	
20	5,21	10,41
40	5,86	12,75
60	6,62	13,57
80	7,68	15,06
100	8,05	16,15

From the obtained data it was found that laser leather training changes its ability to adsorb water vapor and desorb moisture into the environment. Depending of nature frequency radiation and the nature of its interaction with the leather, these changes are differen. In this case, the unequal position of the prototypes from a hygroscopic point of view was revealed.

Analyzing the obtained data it was determined that in the experimental radiated leather sample an increase in water affinity is observed due to hydrophilic groups of amino groups of leather collagen. For the same reason, the desorption of water vapor in the control leather is slower

By decrease, the laser beam will be additionally affected by the decomposition of non-collagen proteins and other concomitant carbohydrates, lipids, etc. on the facial surface of the leather in the form of globular formations in the structure of the leather to decrease the adsorption ability of a prototype leather sample.

At the expense of selective frequency of the spectrum laser on the front surface of the leather, an unexpected increase in the number of small pores appeared, which ultimately would contribute to an increase in the rate of moisture condensation in them.

Deserves attention is fact that we have established that in a moisture-saturated atmosphere, control leather significantly absorbs moisture. When lowering the relative humidity of the environment decreases, the samples intensively desorb moisture. Shoes made of such materials will more absorb the moisture released by the foot of a person and emit rather quickly into the external environment.

Comparing the sorption ability of experimental and control leather images, we can conclude that the leather sample subjected to radiation has better hygienic properties. It should also be noted that by conducting optimal laser irradiation of the leather, the necessary properties of the leather can be provided.

IV. CONCLUSIONS

Carried laser modification of a sample of the surface of natural leather was performed using a laser generating in a double-pulse mode (pulses are separated by a time interval of 3 µs, pulse duration of 10 ns) with a wavelength of 1064 nm with an input energy of 5-40 J and exposure time in the range of 5-40 s. The features of laser modification in the dual pulse mode to the surface morphology of natural leather are established. It has been revealed that elastin fibers change significantly during laser radiation. The amount of moisture adsorbed by experimental leather samples in an atmosphere with different relative humidity was determined. It has been established that a decrease in the adsorption capacity of a leather prototype occurs due to laser radiation and will additionally affect the decomposition of non-collagen proteins and other associated carbohydrates, lipids, etc.

REFERENCES

1. Voznesensky E.F., Khasanshin R.R., Krasina I.V., Abdullin I.Sh., Safin R.R., Aminov L.I. General principles for the modification of natural fibrous materials of various origin in the plasma of a low-pressure RF discharge // Bulletin of Kazan Technological University. -2009,- №1,- P. 304-307.
2. Tikhonova N.V., Abdullin I.Sh., Mahotkina L.Yu. High-frequency low-pressure plasma in shoe production // Bulletin of Kazan Technological University. -2009,- №1/5,- P. 131-136.
3. Kulevtsov G.N. Improving the efficiency of the use of low-grade raw materials in leather and fur production using high-frequency plasma: scientific foundations and technologies : Abstract dis. ... doc. tech. Sciences: 05.19.05. Kazan, 2009, p. 24.
4. Abdullin I.Sh., Zheltukhin V.S., Borodaev I.A. Modeling the modification of the nanostructure of high molecular materials in low temperature plasma. Materials of the IV International Kazan Innovation Nanotechnology Forum (NANOTECH'2012). Kazan, November 27-29, 2012, Kazan: sue "tatarstan center of scientific and technical information (CSTI)" , 2012, – P. 212-215.
5. Markevich M.I., Zhigulin D.V., Zhuravleva V.I., Stelmakh V.F., Chaplanov A.M. Impact of pulsed laser radiation on basalt fabric // Polymer materials and technologies. 2018, T. 4, № 3, P. 51–56.
6. Adashkevich S. V., Markevich M. I., Malyshko A. N., Zhuravleva V. I., Stelmakh V. F., Chaplanov A. M. Surface morphology and magnetic resonance absorption of microwave energy by foam treated with pulsed laser radiation // Polymer materials and technologies. 2018, T. 4, № 1. P. 27–31.
7. Golovteva A.A., Kutsidi D.A., Sankin L.B. Laboratory workshop on chemistry and technology of leather and fur.- M.: Legprombytizdat, 1987, (Russian). 311 p.
8. Greg S., Sing K. Adsorption, specific surface area, porosity. Under. ed. K.M. Chmutova. –(Russian).: World, 1970, 108 p.
9. Sysoev V.A. Chromium-saving technologies for the preparation of semi-finished fur products using non-isocyanate urethanes and plasma treatment. : Abstract of diss. ... doc. tech. Sciences: 05.19.08.- Kazan, 2006, 32 p.
10. Krasina I.V. Regulation of the properties of natural high molecular weight fibrous materials using non-equilibrium low-temperature plasma in the processes of leather and fur production. 05.19.05 - Technology of leather and fur. Abstract of diss. ... doctor. technical science. Kazan. -2006, 34p.
11. Kulevtsov G.N. Improving the efficiency of using low-grade raw materials in leather and fur production using high-frequency plasma. 05/19/05 - Technology of leather and fur. Abstract of diss. ... doctor. technical science. Kazan. -2009, 32 p.
12. Markevich M.I., Chaplanov A.M. Structural transformations in thin metal films under pulsed laser irradiation // News of the National Academy of Sciences of Belarus. Series of physical and technical sciences. 2016, B. № 1, P. 28–34.
13. Mukhametshin A.M. Development of technology for soaking-ash and tanning processes in the production of chrome leathers using non-equilibrium low-temperature plasma of low pressure. : Abstract dis. ... cand. tech. Sciences: 05.19.05. Kazan, 2007, p. 22.
14. Brown E.M. Collagen – a Natural Scaffold for Biology and Engineering // Journal of the American Leather Chemists Association. VOL. 104, 2009, –P. 275-285.
15. Kodirov T.J. Means and methods of collagen research. Monograph. Ed. FAN. MCHJ Yosh heap-press mathboti. June 2014, T. 386 p.
16. Dzhuraev A.M., Kodirov T.J., Toshev A.Yu. The study of nano-amorphous-crystalline phases of hydrophobized leather by x-ray structural analysis. "Technique va technology larni modernization lash sharoitida and ктidorli oshlarning innovation ғoyalari va islanmalari" ilmiy-amaliy anzhumani. Toshkent. TTESI 23-24 апрель 2014, –P. 259-261.
17. Dzhuraev A.M., Akhmedov V.N., Kadirov T.J., Toshev A.Yu. Ramazonov B.G. study of the distribution of polymers on the inner surface of the leather..// Timachilik muammolari magazines. 2007, T. № 3, –P. 65-70.
18. Akhmedov V.N., Dzhuraev A.M., Toshev A.Yu., Kadirov T.J., Khudanov U.O. Study of the kinetics of water displacement with some solvents from the inner surface of the leather. // Journal "Reports of the Academy of Sciences of the Republic of Uzbekistan", 2007, № 6, –P. 62-65.
19. Kodirov T.J. Collagen nanostructure. Ed "FAN". Tashkent. 2015, 537 p.

AUTHORS PROFILE

Kodirov T.J Tashkent Institute of Textile and Light Industry, 100100, st. Shohzhahon-5, Tashkent, Republic of Uzbekistan

Markevich M.I Physical and Technical Institute of the NAS of Belarus, ul. Kuprevich, 10, **220141**, Minsk, Belarus

Malyshko A.N Military Academy of the Republic of Belarus, Independence Ave. 220, 2200057, Minsk, Belarus

Zhuravleva V.I Military Academy of the Republic of Belarus, Independence Ave. 220, 2200057, Minsk, Belarus

Sodikov N.A. Tashkent Institute of Textile and Light Industry, 100100, st. Shohzhahon-5, Tashkent, Republic of Uzbekistan