LASER MODIFICATION OF LEATHER AND FUR SURFACE TO IMPROVE ITS QUALITY WHEN CONDUCTING FINISHING OPERATIONS

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Received: 16.07.2020 Accepted: 09.10.2020 https://doi.org/10.24264/lfj.20.4.2

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ABSTRACT. The article discusses the problems of activation of the surface of the leather tissue by laser exposure, changes in the morphology of the surface of the leather tissue during laser processing, and subsequent covering dyeing of the leather. It is shown that laser treatment changes the structure of the surface of the leather tissue, the bundles of collagen fibers are split, the structure becomes loose, which increases the diffusion of the coating dye reagents, and their reactivity increases without chemical modification. In the process of grinding leather fabric, it is finely cleaned which improves adhesion of the coating paint to the surface of the leather fabric, which improves the quality of leather fabric products. It was shown that laser exposure under the conditions found (pulses with an interval of 3 μs, a duration of 10 ns) does not cause destruction and configuration changes in collagen.

KEY WORDS: leather tissue, pigment concentrate, casein, acrylic aldehyde, copolymer emulsion of butyl acrylate, methyl methacrylate and acrylic acid, coating dyes, laser radiation, diffusion, surface structure of leather tissue, collagen fibers, elemental analysis, magnetic resonance, adhesion

MODIFICAREA CU LASER A SUPRAFEȚEI PIEILOR ȘI BLĂNURILOR PENTRU ÎMBUNĂTĂȚIREA CALITĂȚII ACESTEIA LA EFECTUAREA OPERAȚIUNILOR DE FINISARE

REZUMAT. În articol se discută problemele legate de activare a suprafeței pielii prin expunerea la laser, modificările morfologiei suprafeței pielii în timpul prelucrării cu laser și vopsirea ulterioară a pielii. S-a demonstrat că tratamentul cu laser schimbă structura suprafeței pielii, mănunchiurile de fibre de colagen se scindează, structura devine slăbită, ceea ce crește difuzarea reactivilor din coloranți, iar reactivitatea acestora crește fără modificări chimice. În procesul de șlefuire a pielii, aceasta este curățată fin, ceea ce îmbunătățește aderența vopselei pe suprafața pielii, îmbunătățind în cele din urmă calitatea produselor din piele. S-a demonstrat că expunerea la laser în condițiile specificate (impulsuri cu un interval de 3 μs, durată de 10 ns) nu provoacă distrugeri și modificări în structura colagenului.

CUVINTE CHEIE: țesutul pielii, pigment concentrat, cazeină, aldehidă acrilică, emulsie de copolimer de acrilat de butil, metacrilat de metil și acid acrilic, coloranți pentru vopsire, radiații laser, difuzie, structura suprafeței pielii, fibre de colagen, analiză elementară, rezonanță magnetică, aderență

MODIFICATION AU LASER DE LA SURFACE DU CUIR ET DE LA FOURRURE POUR AMÉLIORER LA QUALITÉ DE LA SURFACE LORS DE LA RÉALISATION DES OPÉRATIONS DE FINITION

RÉSUMÉ. L'article traite des problèmes liés à l'activation de la surface du cuir par exposition au laser, aux changements de morphologie de la surface du cuir pendant le traitement au laser et à la teinture ultérieure du cuir. Il a été démontré que le traitement au laser modifie la structure de la surface du cuir, les faisceaux de fibres de collagène se séparent, la structure s'affaiblit, ce qui augmente la diffusion des réactifs dans les colorants, et leur réactivité augmente sans changement chimique. Lors du ponçage du cuir, celui-ci est finement nettoyée, ce qui améliore l'adhérence de la peinture sur la surface du cuir, améliorant finalement la qualité des produits en cuir. Il a été démontré que l'exposition au laser dans les conditions spécifiées (impulsions avec un intervalle de 3 μs, durée 10 ns) ne cause pas de dommages ou de changements dans la structure du collagène.

MOTS CLÉS : tissu de cuir, concentré de pigments, caséine, aldéhyde acrylique, émulsion de copolymère d'acrylate de butyle, méthacrylate de méthyle et acide acrylique, colorants de revêtement, rayonnement laser, diffusion, structure de la surface du cuir, fibres de collagène, analyse élémentaire, résonance magnétique, adhérence

INTRODUCTION

The variety of existing forms of plasma discharges (smoldering, RFE, RFI, arc, laser, etc.) provides this method of processing with a wide and multi-directional application. An analysis of the types of plasma discharges showed the promise of using some forms for processing a leather semi-finished product, with the aim of

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forming a set of new unique characteristics for it to ensure its competitiveness in the world market [1].

The authors of [2] activated the surface of dyed genuine leather using diffuse air plasma treatment. Plasma was generated by a diffuse coplanar surface barrier discharge (DCSBD). It was found that a plasma treatment time of 10 s is sufficient to reduce the contact angle of water from 85° to 45°. Improving wettability is important for bonding stained leather and better adhesion to leather. An X-ray photoemission spectroscopy study showed that the percentage of oxygen-containing bonds responsible for hydrophobicity increases significantly when treated with plasma. The effect of plasma treatment on the mechanical properties of dyed leather was evaluated using tensile strength measurements. No significant changes in surface morphology and mechanical properties were observed. The results showed that the DCSBD method can provide the high throughput, technical simplicity and economy required by the leather and fur industry.

Currently, the problems of improving the quality of domestic products are relevant. Quality requirements for leather products include not only strength properties, but also an attractive appearance. The quality of products can be improved by creating new materials or giving them new properties by modifying them [3-5]. One of the promising areas for the modification of genuine leather is its processing by laser radiation. The advantage of this method is that it allows you to change the structure of surface layers [6-7]. Such processing is one of the new technologies that allows you to create leather materials with desired characteristics. Cover dyeing of leather fabric is the main finishing process of the technology. The leather then acquires a good appearance and defects in leather fabric hide. Laser exposure allows you to purposefully change the structure and thereby change the properties of natural materials. This technology relates to environmentally friendly processing methods.

The purpose of the work is to establish the features of laser modification of the surface of the leather tissue in the dual pulse mode on the morphology of the surface of the leather tissue in the process of coating dyeing.

EXPERIMENTAL PART

Objects of Study

Leather

Leather is a strong, flexible and durable material obtained by dressing hides in a traditional economy or industrial enterprise. A separate category is fur production. Leather is used in various fields, from the production of shoes and clothing to the binding of books and the manufacture of furniture upholstery and leather wallpapers. Many varieties of leather with various properties are produced. Most often, under these concepts of cattle or small cattle, all types of classical smooth or embossed, but not exotic leather, are meant. Namely, in everyday life for cattle or small cattle - the leather of a cow, bull, buffalo, calf, goat, sheep, lamb, etc.

Cattle skin - the leathers of castrated gobies weighing more than 17 kg in pairs. Depending on the mass, the calf is divided into two groups: light calf - weighing from 17 to 25 kg inclusive, heavy - weighing more than 25 kg. The thickness of the calf is not the same: in the rump 3.5–5.5 mm, in the head 2.5–4.5 mm, in the floors 2-3 mm. With a mass of 17-19 kg, the area of the bovine reaches 300 dm^2, with a mass of more than 30 kg - 500 dm^2. The leathers have a length of 1.75 to 2.4 m, and a width of 1.5-2 m.

Fur Sheepskin

Leathers of adult and semi-adult sheep of fine wool, semi-fine-wool and semi-coarse-haired breeds, as well as crossbreeds, are referred to the fur sheepskin. In this regard, distinguish fine-fleece, half-fine, semi-rough sheepskin.

The production of fur sheepskin comes in approximately the following proportions,%: in terms of wool - wool and half-woolen 88.1, low-wool 11%; by canning methods - wet salted and acid-salted 65.1; dry-salted and fresh-dry 34.9;

according to the fineness of the hair - fine-fleece 19.8, half-fine-crowned 67.3, semi-rough 12.9; by grades - I - 10.1, II - 28, III - 44.4, IV - 17.5.

The quality of the sheepskin depends on the breed, age, conditions of keeping, feeding the sheep, as well as on the quality of the primary processing of sheepskin. Fur sheepskins are characterized by large sizes, their weight varies depending on the degree of contamination, quality of removal, degree of humidity, length and density of wool.

Chrome Tanned Leather

For the study, unpainted chrome leather wastes were used, with the following physicochemical parameters. In %: humidity - 52.4; total ash - 4.8; fatty substances - 3.2; Goal substance - 76.83; chromium oxide - 5.2; and hydrothermal destruction of 92.0 °C.

Methodology and Research

Laser Radiation

In this work, we used laser processing in the regime of double pulses of a sample of genuine leather. An LS-2134D yttrium-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). The sample was treated with laser radiation in the energy range 5–40 J at exposure times of 5–40 s [8].

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 [9].

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 ($MgO{\cdot}Mn_2^+$) [8].

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) [8, 9]. The sample was treated with laser radiation in the energy range 5–40 J at exposure times of 5–40 s. According to [4–5, 7], the evaporation of matter occurs under the influence of the first laser pulse, and a region with an increased temperature and a lower density of air particles forms in the surface layer, which leads to a more complete use of the energy of the second pulse for laser ablation [8].

The study of the surface morphology of leather tissues was studied 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 the chemical elements of the sample, and also obtain an image of the object in a wide range of magnifications.

The leather tissue of the fur was also investigated. The thickness of the leather tissue sample is 1.2 mm.

Figure 1 shows the structure of the leather tissue before laser exposure.

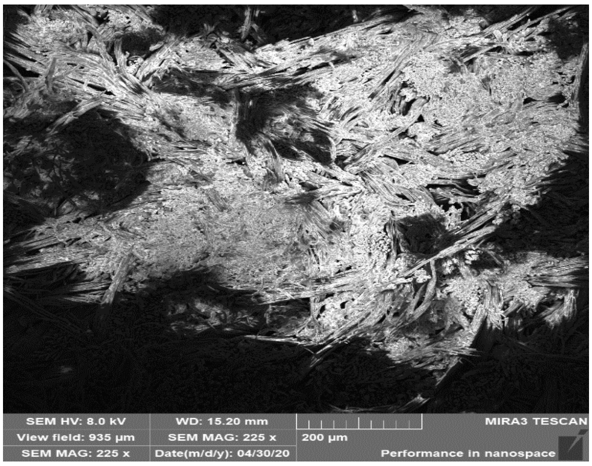


Figure 1. The structure of the leather tissue before laser exposure

From the figure it was established that the structure of the dermis is dense, collagen fibers are adjacent to each other. Moreover, the pore size varies from 20 to 70 microns.

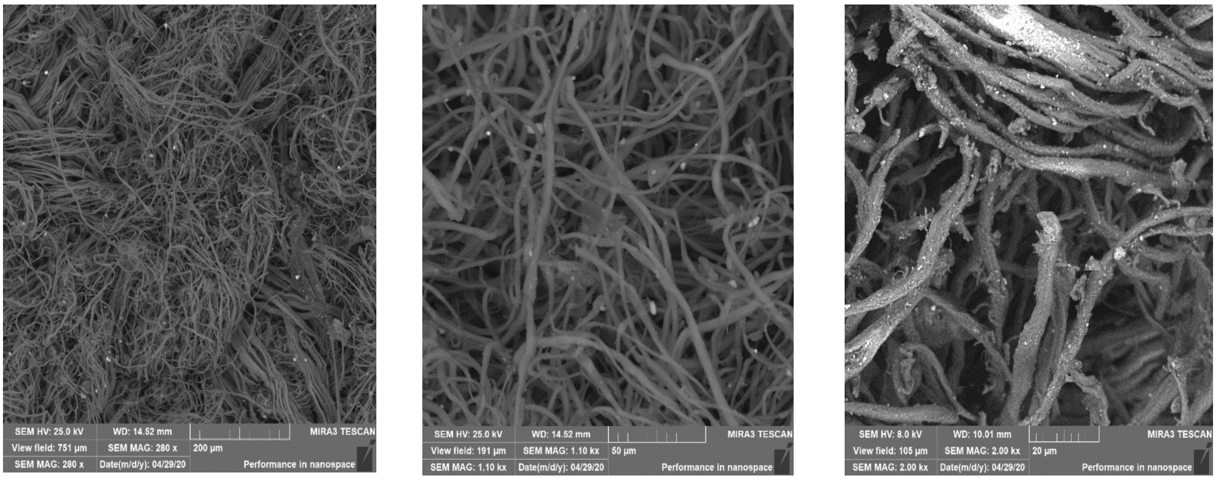


Figure 2. The surface structure of the leather after laser exposure (t=40 s; E=40 J)

From Figure 2 it follows laser irradiation, changes in the structural elements of collagen bundles occur, the structure loosens, the surface relief changes, smoothest. From Figure 2, it follows that the thickness of an individual collagen fiber varies from 2.5 to 5 µm. A comparative analysis of the structure of the leather tissue before and after laser treatment shows that it leads to the splitting of bundles of collagen fibers and changes in the microstructure, which are expressed in the breaking of weak inter fibrillar hydrogen bonds, which contributes to an increase in chemical activity during further covering staining of the leather tissue due to the formation of free radicals (see Figure 3).

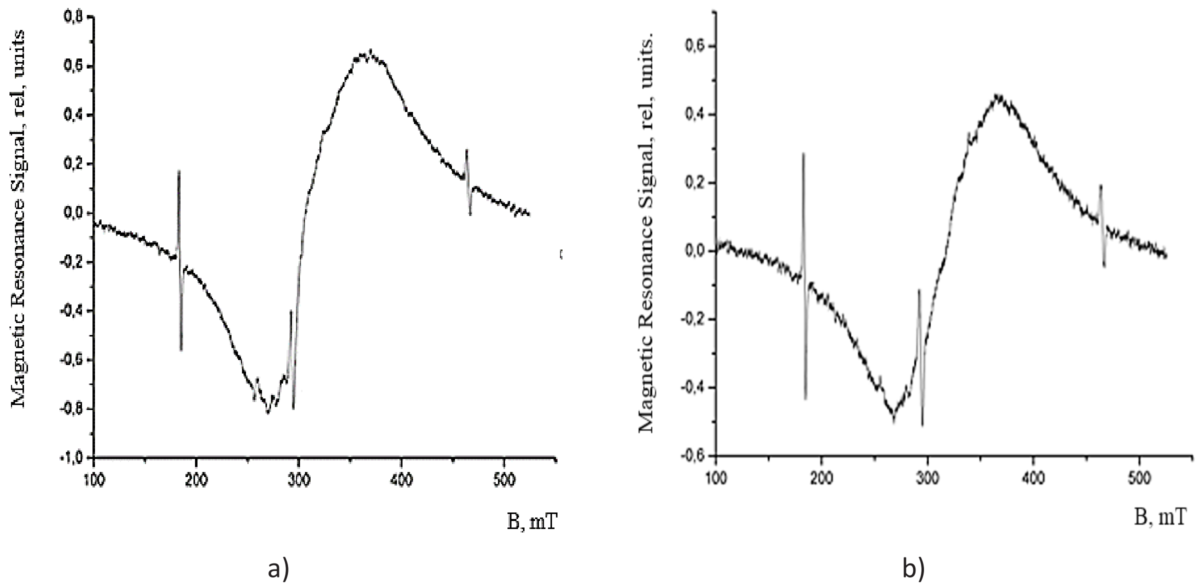


Figure 3. EPR signal for a sample of leather tissue before (a) and after (b) laser irradiation (energy input 40 J, exposure time 40 s).

An inhomogeneous broadened resonance line with effective g-factor values of 2.3 ± 0.1 and a line width of 96 mT after laser irradiation is recorded on the magnetic resonance spectrum. The wide line after laser exposure indicates the activation of the surface and the chemical activity of the leather tissue for further processing.

In addition, in the process of laser resurfacing, leather tissue is cleaned, which also contributes to improved adhesion during subsequent coating dyeing of the leather.

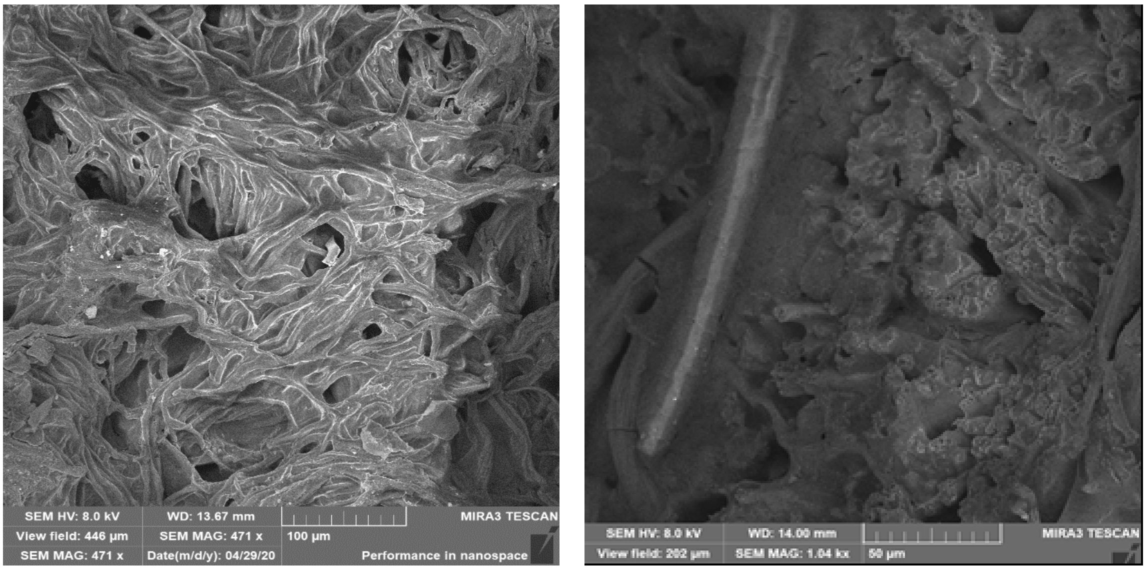
Coatings that are used to finish leather fabric are divided into 4 groups, determined by the type of film former [10-12]: nitrocellulose, acrylate and protein, polymerization (emulsion or latex). None of the film formers are used in their pure form. This is because each of them, along with positive properties, has a number of disadvantages that do not allow creating a coating with a full range of useful properties [13].

In accordance with the technology of coating dyeing, the leather tissue was coated using a copolymer emulsion of butyl acrylate, methyl methacrylate and acrylic acid neutralized with ammonia to pH = 7.0-8.0 with the addition of polyhydrosiloxane - GKZh-94 as a hydrophobizing agent.

The ratio of the components of the film-forming composition was calculated based on the dry residue of the film-forming agent and the pigment content in the coating concentrate. The concentration of pigments in coating compositions ranged from 5 to 10 parts by weight. From the mass fraction of the polymer, namely 5, 6, 7, 8, 9, 10 parts by weight.

Upon receipt and study of the properties of coating compositions, the problem was solved to improve the adhesive properties during long-term operation of the products. The coating compositions studied included a pigment concentrate, casein, acrylic aldehyde, a copolymer emulsion of butyl acrylate, methyl methacrylate and acrylic acid (in a ratio of 35.37: 46.68: 17.95, respectively).

Figure 4 shows the morphology of the surface of the leather tissue after laser exposure and coating dyeing (at various magnifications).



a) b)

Figure 4. The morphology of the surface of the leather tissue after laser exposure and coating dyeing

As can be seen from Figure 4, topcoat dyeing of leather tissue decorates and slightly changes its appearance. In the process of painting, the fibrils are glued together, the size of the bundles varies from 12 to 40 microns. Figure 5 shows the elemental analysis of skin tissue after laser treatment and coating dyeing. Black topcoat was applied to the surface of the sample 2 times, and after drying, further research was conducted.

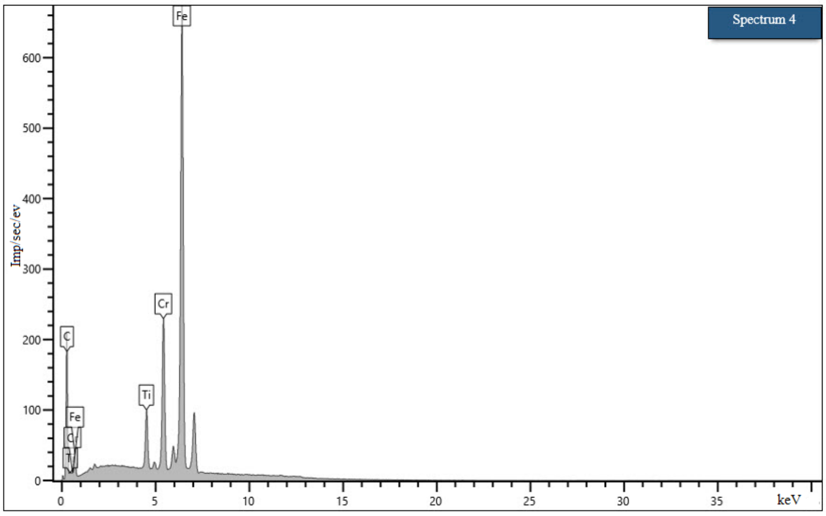


Figure 5. Elemental analysis of skin tissue after coating dyeing

Table 1: Spectrum results depending on the ratio of elemental analysis

№	Result Type, Spectrum Label	Spectrum 4, mass /%
1.	C	41.25
2.	Ti	3.08
3.	Cr	9.91
4.	Fe	45.76
	Total	100.00

As can be seen from the analysis (Figure 5 and Table 1), Ti, Cr, Fe are present on the surface of the sample.

The results of the study of the influence of the chemical nature of the coating dyes on the gasoline resistance of a multilayer coating of leather tissue are presented in Table 2.

Table 2: Coating adhesion coating dyeing obtained at room temperature

Index	Laser free impacts	After laser impact
The amount of swelling of the sample in gasoline for 2 hours, %	82	24
Adsorption of water, ml	0.33	0.46
Adhesion, N/m		
in gasoline	548	813
in dry condition	2148	2578

Analyzing the data obtained in the table, it can be noted that the proposed samples treated with a coating dye after laser exposure form films having almost four times less swelling than samples treated with a coating dye without laser exposure. Reducing the amount of swelling of the lower coating layer reduces the amount of swelling of the coating as a whole, which possibly slows down the further diffusion of gasoline, and thereby reduces its accumulation at the skin-fabric coating interface and reduces the wedging effect of the aggressive environment. This is facilitated by the better compatibility of the coating dyes with the front surface after laser exposure. The value of the adhesion of the coating and its gas resistance, along with the indicated factors, can be associated with the interaction of the laser exposure of the skin tissue with the coating dyes.

CONCLUSIONS

Laser modification of a sample of the surface of the skin tissue was performed using a laser generating in a double-pulse mode (pulses separated by a time interval of 3 µs, pulse duration 10 ns) with a wavelength of 1064 nm with an input energy of 5-40 J and an exposure time of 5-40 s followed by a coating dyeing. It was shown that laser treatment changes the structure of the surface of the skin tissue, the bundles of collagen fibers are split, the structure becomes loose, which increases the diffusion of the coating dye reagents, and their reactivity increases without chemical modification. In the process of grinding leather fabric, it is finely cleaned, which helps to improve the adhesion of topcoat paint to the surface of leather fabric, which will improve the quality of leather fabric products. It is shown that laser exposure under the conditions found does not cause destruction and configurational changes in collagen.

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