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Design of Special Purposes Products Made of Nanomodified Leather

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ABSTRACT

The most notable changes in shoes during use occur in its volume and upper. Thus, by bearing on foot beams, bending in the metatarsophalangeal joints, they widen in this area. At that, footstep changes the position and pushes against the shoe upper parts, which stretch and then shrink. All these multiple deformations cause the wear of the shoe upper parts. The quality of a product and consumer characteristics of uppers material depend on the adhesive strength of the leather coating and the properties of coating compositions. The priority of improving the leather properties is high-frequency (HF) low-pressure plasma processing. Samples of buffer dry leather and grain leather were subjected to high-frequency plasma treatment under reduced pressure by using a radio frequency (RF) plasma with a discharge power (P) of 0.2 to 1.8 kW and a duration of exposure (τ) up to 7 min. The analysis of morphological changes of nano-modified leather structure was carried out using multifunctional Rigaku SmartLab X-ray diffractometer. Research results show that RF-plasma treatment increases the adhesion of the coating film to the leather uppers and resistance to abrasion and repeated bending of uppers, which define the ability of material to preserve its consumer properties and characterize longer safety of special purpose footwear form during its wearing.

KEYWORDS
Personal protective equipment, special-purpose footwear, nanomodified leather, adhesive strength, radio-frequency plasma.

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Introduction

Textile industry is a significant multiple-discipline sector of the economics, which influences on the stable and balanced social and economic development of the country and provides an independent and intellectual levels of the society.

From the branch work effectiveness point and taking into account of situation around the external economic rate huge and massive tasks connected to the renew of high-quality production and continuous process of labor protection improvement need to be solved by the domestic producers (Nikitina, Makhotkina & Fukina, 2010; Bekk, Belova & Makhotkina, 2012; Zakirova &

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Purik, 2016). High productivity of labour is not only the result of interaction of human, nature and technique but also right organized labor activity.

Physical activity and capacity for work of the specialist is provided by the rationally chosen equipment. Enterprises provide their workers with means of individual protection, which include garment and footwear of special purpose. Means of individual protection protect from adverse impact during the operation of work (Rehani, 2015). The main aim of use of means of individual protection is prevention of industrial injuries.

Garment and footwear of special purpose are operated in severer industrial conditions than domestic. Because of this the construction and technology of garment and footwear of special purpose have specific features. The level of deterioration of uppers materials are determined by physical activity, which in turn is divided into biomechanical determined by anatomical and physiological features of a man and sanitary and hygienic properties connected to the whole or part hygroscopicity of material (Zhikharev et al., 2011). Any means of individual protection, regardless the end use, must be ergonomic, harmless, safe, ensure the unimpeded normal functioning of the human body during the planned period of operation.

Materials used at special purpose footwear production differs a lot from the deterioration of model footwear by character and level of exploitation deterioration and also service life. Character, terms of advent and the intensity of defects development of uppers, lining and bottom of footwear are determined by the sorts and properties of used materials, footwear design, detail disposition and operation conditions or complex of impacts at the operation.

State All-Union standard

Russian leather, yuft of chrome style tanning or dense chrome leather of the leathers of cattle are usually used for the production of external special purpose footwear details (Makhotkina, 2006b). State All-Union standard 3123-78 "Leather production. Terms and definitions" picks out group of leather, which is considered as leather which is operated in severer conditions. That differs this type of leather from model, which is operated in normal nature conditions without taking into account of professional activity and condition of man. Leathers of special purpose are usually used for the production of clothes and footwear for workers of power structures, energy, oil and gas and other complexes.

Considering the operation and ergonomic characteristics of footwear, the most visible changes of area and volume of uppers take place during its operation (Marvin et al., 2015). It is explained by the intensive mechanical influence on it. Forms and sizes of foot vary during the process of work, so forms and sizes of footwear are also varying. By relying on the beams foot, bending at the phalange joints, expands in this area. At this time foot changes its location and press on the uppers details, which stretch, and then shrink (Kozar, Mokrousova & Wozniak, 2014).

Repeated deformations promote the uppers deterioration (Sirazieva, Stepin & Makhotkina, 2004a). In addition, in the toe-beam pert of footwear non-vanishing creases are appeared. This leads to the coating surface defects or through-holes on the uppers materials. Besides the stretches and bindings uppers details are exposed to friction, beats, punctures and other impacts.

Product quality and consumer properties of uppers materials depend on adhesion durability of coating to the leather and depend on properties of coating compositions their selves. Water-soluble polymeric film-forming agents are widely used in methods of protective and decorative finishing of materials surfaces (Ibragimov, Makhotkina & Shaekhov, 2003). Leather coating must satisfy the complex of properties, which are defined by the technology of its production and conditions of operation of products made of it. Coating dye, applied to the face surface of leather, penetrates to the elastic porous structure of the papillary layer and must forms the coating which joins the high elasticity with enough durability (Dojan, Johnson & Kohatsu, 2013).

The product quality and consumer characteristics of uppers material depend on the adhesive strength of the leather coating and the properties of coating compositions. The most widely used methods for protective and decorative surface finishing materials are water-borne polymeric film formers (Makhotkina, 2006a). Leather coatings must comply with the complex of properties, defined by their production technology and conditions of use of these products. Pigment, applied to the front leather surface, penetrates the porous elastic papillary layer and must form a coating that combines high flexibility with sufficient strength (Makhotkina & Khristoliubova, 2014; Makhotkina & Khristoliubova, 2015). The priority of improving leather properties, surface properties of uppers materials and the adhesiveness of buffer and natural leather is its treatment with high-frequency (HF), low-pressure plasma (Sirazieva, Stepin & Makhotkina, 2004b; Osin et al., 1998).

Method

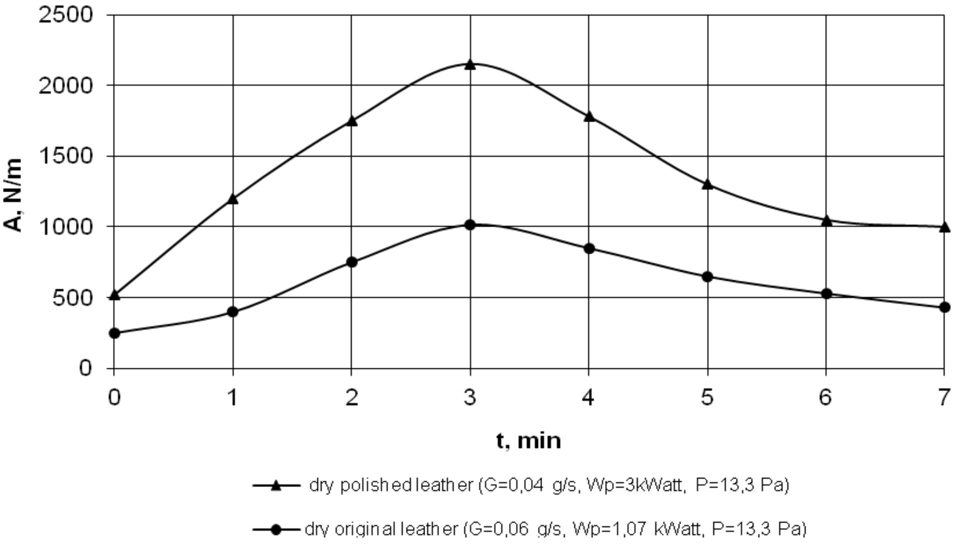
Samples of buffer dry and grain leather were subjected to high-frequency plasma treatment under reduced pressure by using a radio frequency plasma (RF) with a discharge power (P) of 0.2 to 1.8 kW and a duration of exposure (τ) up to 7 min.

Analysis of morphological changes of nano-modified leather structure was carried out using multifunctional Rigaku SmartLab X-ray diffractometer. Diffraction were measured in a parallel beams scheme at grazing incidence mode (incidence angle = 3°) at angles ranging from 30° to 55° in 0.02° increments and record time at each point was equal to 3 sec. Incident beam slots: 5,0° (Soller slit), 0.7 mm (divergence slit). Diffracted beam slits: 5,0° (Soller slit), 0,7 mm (anti-scatter slit). Software processing of diffraction patterns was performed based on $K\alpha1$ and $K\alpha2$ lines overlap and without taking into account the equipment function. Wavelength of $CuK\alpha1 \approx 1.5406$ Å.

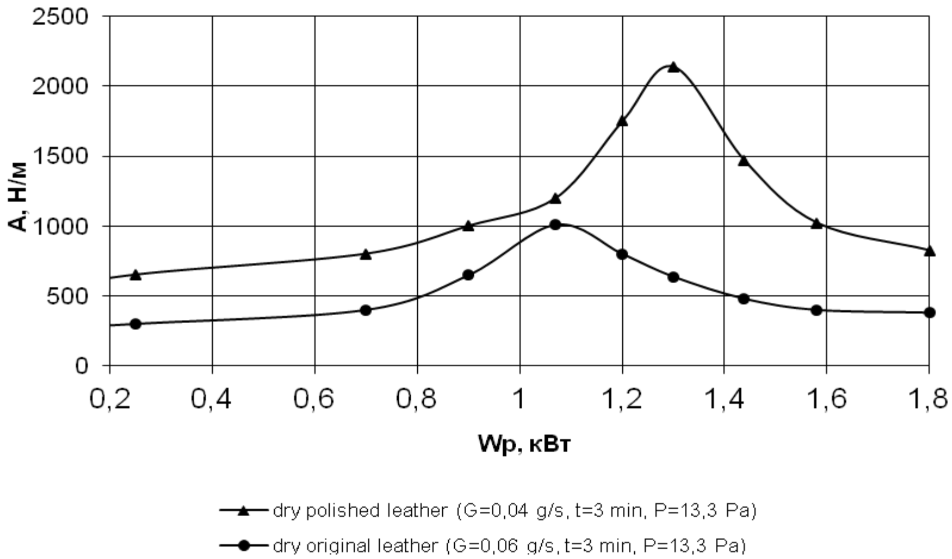
In order to study the structural changes in the dermis layers, leather sections were examined through electron microscopy (Osin et al., 1998). The combination of these methods allowed to see the basic changes in the leather structure for shoe uppers and determine the effect of the gas discharge parameters on the range of these changes.

Data, Analysis, and Results

Polished and original leather was activated by the radio-frequency plasma (RF) of low pressure to increase surface characteristics of uppers materials and adhesion (Makhotkina, 2006a; Makhotkina & Khristoliubova, 2014). Modification of the coating film adhesion during the surface treatment of polished and original leather by the RF-plasma is shown in Figure 1. Coating adhesion to the leather increased in 3-4 times after the 3 minutes treatment (Figure 1(a)). Coating adhesion to the leather with origin face surface increases as the power of the charge increases up to 1.07 kWatt (Figure 1(b)); to the polished leather as the power of the charge increases up to 1.3 kWatt (Makhotkina & Khristoliubova, 2015).



a)



b)

Figure 1. Modification of adhesion to the modified leather depending on: a) time of plasma treatment; b) charge power

To define the influence of the RF-plasma stream to the acryl film the following researches were carried out. A film without being applied to the leather was treated by the plasma.

Plasma treatment leads not only to the modification of interaction of film and leather but also to the structure modification of the film itself. According to the data of the Table 1 adhesion durability of coating film after the RF treatment for original and polished leather increased, especially in a dry condition. At the same time tensile strength was increased by 15-20%.

Table 1. Coating adhesion durability to the original and polished modified leather

Leather type	*Adhesion incensement in times*	
	Dry condition	Wet condition
Original leather with emulsion	3,7	2,4
coating	1,5	1,3
Polished leather with emulsion coating	4	3,2

Due to the fact that the material properties are directly dependent on their structure, the authors conducted an analysis of the structural changes under the influence of high-frequency plasma treatment.

Structural changes of nano-modified natural grain and buffer coated leather before and after the plasma treatment are shown in Figure 2.

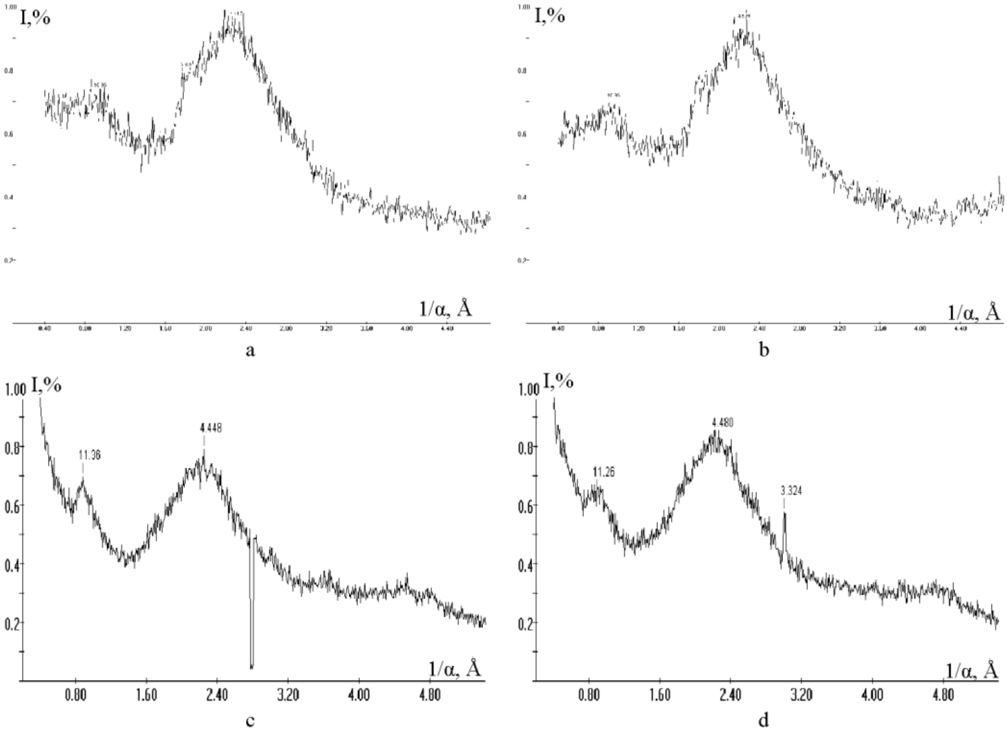


Figure 2. Diffraction curves of grain leather before (a) and after plasma treatment (b) and buffer coated leather before (c) and after plasma treatment (d)

In the diffraction patterns of grain leather (Figure 2a, b), the maxima at 10-11A 4-5A characterize the presence of two amorphous objects that differ in average interatomic distances. Moreover, while the first maximum at 10-11A shows the homogeneity of this phase, the second maximum at 4-5A due to its complex shape (presence of "grades") indicates its heterogeneity. Both phases are organic in nature. They differ in the values of interatomic distances (Sirazieva, Stepin & Makhotkina, 2004b).

Diffraction patterns of the buffer coated leather (Figure 2 c, d) shows that the amorphous phase is present on both the treated and non-treated coated leather sample, but crystalline phase was observed only in the treated sample. The amorphous phase of the initial sample can also be determined by the presence of two broad diffraction maxima with d = 11,5-10,5 Å and 4,7-4,5 Å. The grade of structural perfection of the amorphous phase in the diffraction pattern developmental prototype is higher, compared to a check one. This is evidenced by the appearance of additional weakly conspicuous broad maxima in 5,7-5,6 Å and 3,8-3,7 Å.

The crystalline component of the treated buffer leather sample can be determined by the presence of narrow diffraction peak with d = 3,324 Å. Reduction of the diffraction maximum half-width (Table 2) indicates an increase in the degree of crystallinity of the amorphous component of the test sample.

Table 2. The results of determining the range of the diffraction maxima, based on the background component (buffer leather)

Samples	*Diffraction maximum range, st. units*
Check	2,151
Treated	1,987

Analysis of buffer leather diffraction patterns allows to conclude that plasma treatment increases the crystallinity of amorphous phase, as related to an untreated sample.

Figure 3 shows photographs of buffer leather sample sections, coated with plasma before and after treatment, as well as the leather.

The pictures shown in Figure 3 suggest that after exposure to RF-plasma, morphological changes occur in buffer leather throughout the leather section thickness.

Non-treated with plasma sample of buffer leather has a uniform, bumpy surface, where one can trace the nature and arrangement of collagen bundles and fibers (Figure 3 a, b). The average angle of inclination of the fiber bundles to the dermis surface at different sections varies, one can see interfascicular space uniformly distributed over the section area. Before the exposure to the plasma, fibers are wavy, neither strained nor tense. After RF-plasma treatment, beams gain strength, their direction becomes more definite.

Leather becomes more elastic and resistant to bending stresses. The completeness of fiber bundles also changes. At a magnification of 500 times, the treated layer shows the thickened arrangement of fiber bundles throughout the buffer leather section thickness.

From Figure 3 (c, f) it can be seen that during the plasma exposure morphological changes occur in emulsion coating which has already appeared on the buffer leather. Coating on the leather check sample surface, in fact does not repeat the leather structure and creates a thick monolithic film, which adversely affects the adhesion of the leather coating (Figure 3 c). After exposure of coated buffer leather to plasma, we can clearly see the averaging of pore size (Figure 3 f), a more clearly defined surface texture, therefore, the contact area of leather surface with the film increases, so the leather coating becomes thinner.

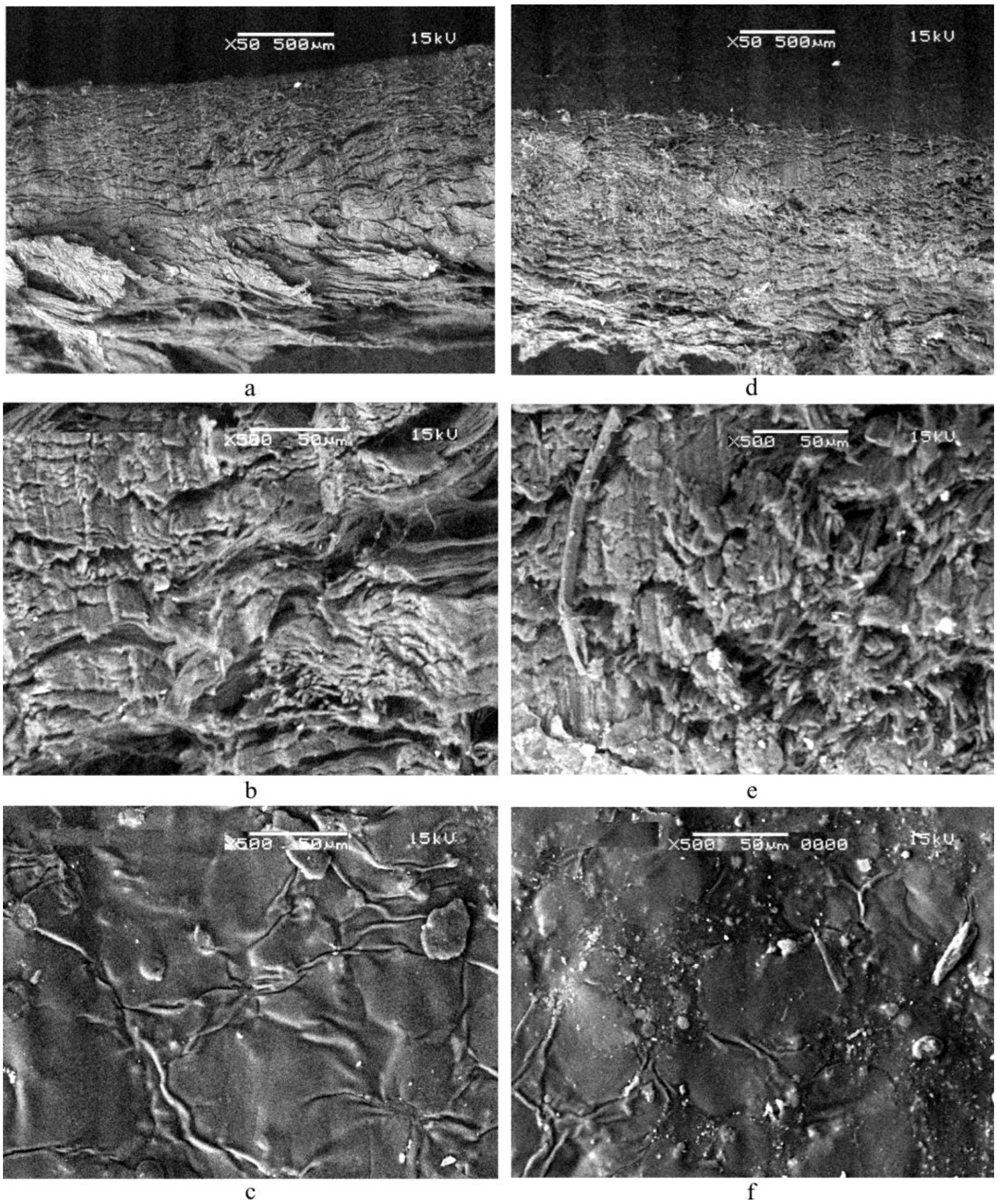


Figure 3. Images of cross section of buffer leather check sample (a-×50, b- × 500), surface (c-×500) and the HF-treated sample (d-×50; e-×500), surface (f-×500)

Research results shows that RF-plasma treatment increases the adhesion of the coating film to the leather uppers and resistance to abrasion and repeated bending of uppers, which define the ability of material to preserve its consumer properties and characterize longer safety of special purpose footwear form during its wearing.

Discussion

To analyze the patterns of exposure to plasma surface dyeing of leather, the researchers determined the mechanical performance of leather, as the performance characteristics, being one of the main features, characterizing the quality of finished leather and determine their functions (Makhotkina & Khristoliubova, 2014; Makhotkina & Khristoliubova, 2015). RF-plasma treatment leads to an increase in most mechanical properties of leather after application of emulsion coating (Table 3).

Table 3. Influence of plasma treatment on the performance of nano-modified emulsion-coated leather for a - grained leather, b - natural leather

Criteria	*with HF-plasma*		*without HF-plasma*	
	a	b	a	b
Tensile strength, MPa	17,0	18,4	14,7	15,2
Tension at occurrence of cracks on the surface layer, MPa	16,2	17,7	13,9	14,5
The elongation at a stress of 10 MPa,%	35	35	36	37
Resistance to multiple bending of coating, points	4	4	3	3
Adhesion of coating film N / m				
- to dry leather	920	2433	230	656
- to wet leather	421	887	133	371
Abrasion resistance, turns	60	50	50	40

When exposed to RF-plasma, the tensile strength of leather increased by 10-20%, the surface layer strength by 10-20%, coating resistance to flexing by 35%, abrasion resistance by 20-25%.

Conclusion

Thus, as a result of plasma treatment of leather, both the buffer front surface and the natural have morphological changes of leather and film structures at the same time, resulting in improved adhesion of leather coating up to 4 times. This is due to the high-frequency plasma treatment which, being three-dimensional, allows the plasma effect, both over the entire coating volume and the leather volume. Changes in the structure, pore averaging and, consequently, arranging the contact surface of contacting polymers causes the coating penetration deeper into the leather and becoming less thick, still retaining its solidity, thereby significantly increasing the adhesion of leather coating.

Disclosure statement

No potential conflict of interest was reported by the authors.

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