Improvement of technical purpose materials performance characteristics with the radio frequency low pressure plasma

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Abstract. The main aim of the work is to solve the actual problem of increasing the competitiveness of tanning products by reducing the prime cost and improving the quality of finished products due to the increased durability of the working elements of tanneries. The impact of the low pressure radio frequency (RF) plasma in the processes of treating for modification of the materials for special purposes is considered in the article. The results of working elements of tanneries and the materials for special purposes sample processing by a RF low pressure plasma are described. As a result of leather materials nano structuring and nano modifying physical, mechanical and hygienic characteristics were increased. Processing of the technical purpose materials allows to increase operational performance of products and extend their lifespan.

1. Introduction

The production of competitive products and the assurance of the release of guaranteed high quality materials of light industry through the introduction of modernized technologies is an integral part of increasing the production efficiency of the textile and light industries. Conditions that ensure the increase of an efficiency in the production can be achieved through technological re-equipment, improving of the quality of raw materials and reagents and carrying out of organizational measures [1-5]. One of the main reasons for the technical and technological backward trend of the leather industry from foreign countries is the low working capacity of the equipment used. A worn and technically obsolete machinery and equipment park is not able to produce a modern assortment of high-quality competitive products. In the leather industry, it is especially important to modernize the equipment for technological operations of planing, breaking and smearing of genuine leathers, which are carried out on planing, milling and breaking machines. At the same time, the quality of planing, skinning and breaking up of leather fabric is determined not only by the properties of the material of the processed semi-finished product, but also by the performance characteristics of the tools (spiral, disk, center, and knife-edge knives), knife-surface grinding regimes along the generatrix, and parameters of the grinding device. In this case, in connection with this, it is necessary to have a scientific justification for the sharpening of the surface of the knives along the generatrix and the optimal design of the grinding device. Recently, complex studies of the system "grinding machine - knife shaft, disk (spiral) knives - a processed semi-finished product" are aimed at providing the required quality of the produced leather while optimizing the physical and mechanical characteristics of tools, increasing the resistance of spiral and disk knives, which, in turn, determines the performance characteristics of the quality of the milling and planing equipment and the productivity of the machinery of production.
Problems of improving the quality of tanning materials during mechanical operations have been considered for a long time [6-8]. A review and analysis of the studies carried out in this direction show that it is necessary to create applied methods for increasing the quality and durability of the working elements of tanneries.

The work is aimed at solving the actual problem of increasing the competitiveness of tanning products by reducing the prime cost and improving the quality of finished products due to the increased durability of the working elements of tanneries.

2. Results and discussion

To investigate the effect of the interaction of a RF low pressure plasma with the material surface of tanneries equipment the experiment was performed in an inert gas plasma, argon, 0.06 g/s and in a mixture of a plasma chemical gas, methane, 0.004 g/s and argon, 0.06 g/s. The working pressure in the chamber is 24-26 Pa. For the deposition of a diffusion protective coating it is necessary to conduct preliminary cleaning and surface activation in a RF plasma of a capacitive discharge. Surface treatment with argon ions with an energy of 60-80 eV made it possible to reduce the surface roughness parameter from 0.4 to 0.19 μm, which in turn increases the quality of the workpiece itself.

Characteristics of a plasma RF generator: power consumption 3.5 kW, output frequency 13.56 MHz. In order to concentrate the electric field near the surface an additional negative potential of -20 V was applied to the product. The processing time was ~ 40 minutes in total: 20 minutes in argon, 20 minutes in a mixture of gases, inert and plasma chemical.

To determine the physical and mechanical properties the microhardness, roughness, elastic modulus and elastic recovery coefficient a scanning nano-hardness meter "NanoScan-3D" was used [9]. Hardness measuring is implemented on the analysis of the dependence of a load when indenter is pressed into the surface of the material on the depth of introduction of the indenter. This method is based on the ISO 14577. The indenter of Berkovich type is used which is a triangular diamond pyramid with an angle at the apex of about 142º. During the dynamic indentation the indenter is pressed into the surface of the sample at a constant speed, when the specified load is reached, the indenter is retracted in the opposite direction. The values of the load and the corresponding displacement of the indenter are recorded. Feature: piezoelectric resonance cantilever with tuning fork with high flexural stiffness of the console (~ 2·10^4 N / m).

Change of the properties such as hardness, Young modulus and coefficient of restitution before and after RF low pressure plasma treatment can be seen below along the depth of the formed diffusive coating (Fig. 1.a-1.c).

![Fig. 1. Changes of physical and mechanical properties of tool steel before and after RF low pressure plasma treatment along the depth of the metal sample: a – hardness, b - Young modulus, c - coefficient of restitution.](image)

Characteristics of the center and disc milling drills made of tool steel before and after the treatment were changed as follows: surface microhardness of a control knife 4.25±0.5 GPa, knife with a
diffusive coating 15±4 GPa, roughness parameter of the knife edge is Ra, 2.50±0.5 mkm, knife with a
diffusive layer 0.5±0.1 mkm, groove radius of a cutting edge of a control knife 36±0.5 mkm, knife
with a diffusive layer on a surface 38±0.5 mkm.

Studies have shown that strengthening of the working elements of machining tanneries such as
center and milling drills with a protective coating of carbides and nitrides with a strengthening phase
makes it possible to increase the resistance of working elements to wear and the time of stable
processing of semi-finished products, and also improves the quality of finished leather materials in the
batch by reducing mechanical defects in leather. According to the test results, it is established that the
relative increase in the area of hides during the cutting with experimental knives is more smoothed and
ranges from 30 to 40%, and for serial knives from 10 to 45%. Evaluation of the cutting quality was
carried out by an organoleptic method and it was established that the sheepskin leather fabric achieves
sufficient plasticity in all directions with an increase in area from 25 to 40%, with a relative reduction
in area below 25% a repetition of the hides is necessary.

The research of the properties changes of leather samples treated with low pressure RF plasma was
carried out on an experimental samples using two technologies: nanostructured samples (genuine
leather of a cattle, which at the final stage of finishing production was treated with RF plasma of
reduced pressure in the mode Wp = 1.5 kW, τ = 7 minutes), nanomodified samples (genuine leather of
a cattle at the final stage of fatliquoring on the top size and dyeing, at step of the fixer deposition
coating film two-fold biocidal agent of silver nano solution of 0.2% was injected and at the finishing
production the samples were treated by RF plasma in a reduced pressure mode Wp = 1.5 kW, τ = 7
minutes).

For the investigation of the surface and cutting edge structure of leather control samples and
treated with the low temperature RF plasma scanning electron microscope Carl Zeiss evo-40 INCAx-sight was used. The range of the accelerating voltage of the electron microscope during the examining
of the surfaces and cuts of control leather samples processed in low temperature RF plasma and
modified samples in low temperature RF plasma with silver - 0.2-30 kV. The working current range is
0.5 pA - 5 mA.

The physical and mechanical properties of leather treated by low temperature RF plasma and
modified by silver are determined by the properties of the fibers and their mutual arrangement. The
microstructure of the cut-off of the control leather samples is shown in fig. 2.a – 2.e, the cut-off of the
leather samples of cattle treated with low temperature RF plasma - in fig. 3.a – 3.e, the cut-off of the
leather samples of cattle treated with low temperature RF plasma with silver - in Fig. 4.a – 4.e. All the
images were made at magnification of 100, 200, 500, 1000, 2000 times. The edge of the untreated
sample has a homogeneous hummocky surface, where the character of the arrangement of collagen
beams and fibers is observed. The average angle of inclination of fiber bundles to the surface of the
dermis varies in different parts of the dermis. Interfascicular spaces evenly distributed over the area of
the cut are clearly visible. After the interaction of the plasma the regularity of the interweaving of the
structural elements of the leather is not disturbed and the angle of the interweaving of the fiber bundles
that affects the strength, wear resistance and plasticity of the leather is not changed. However, after
low temperature RF plasma treatment the fibrous structure separates. This makes the leather to
become softer and more viscous, the penetration depth of the dyes increases. Samples treated with
silver and low temperature RF plasma acquire a soft, uniform surface due to deeper penetration of
silver. This kind of treatment improves the bactericidal properties the leather.

Thus, as a result of plasma treatment, the maximum changes of a leather properties of a cattle
occur. This is explained by the fact that the plasma treatment is volumetric and allows the plasma to be
effected throughout the volume [10,11].
As a result of nanostructuring and nanomodifying of materials the physical, mechanical and hygienic characteristics of special technical purposes materials samples are increased. Processing of leather materials in the specified ranges of processing conditions in the low pressure RF plasma can increase the performance of products for special use and extend their service life.

Samples treated with plasma were cut with knives also treated with plasma. The edge part of a sample cut with the treated tool was clear without villi and scoring. These features are very important in the furrier’s work when the parts of the products are cut from the skin. No micro cracks are observed on the edge of the sample cut with a knife treated by low temperature RF plasma. The elimination of those cracks is very significant as they lead subsequently to a weakening of the bonding strength of the fibers among themselves and this in turns leads to a decrease in the strength of the material.

3. Conclusions
It is established that processing in a jet RF discharge at a reduced pressure leads to a change in the physical and mechanical properties of metals and their alloys. The effect of the low-pressure RF discharge on the physical and mechanical properties of metals and their alloys depends both on the plasma parameters and on the structure of the material. It has been experimentally established that the change in the physical and mechanical properties of tool steel after exposure to low-pressure jet RF
plasma occurs with a change in the phase composition and the parameters of the crystal lattice on the surface. The physical regularities of the change in the properties of the metal are revealed.

Gasification (carbiding) of surface layers of metals and alloys occurs at a depth of up to 500 nm during the processing time up to 40 minutes, which results in an increase in the strength properties, longevity and service life of the products by a factor of 1.5-2. The developed technological processes of plasma gas saturation of steel made it possible to increase the service life of the products by 2-2.5 times in comparison with the untreated ones, to increase the microhardness of the surface by 25%, and the wear resistance by 20%.

As a result of nano structuring and nano modifying of genuine leather materials itself for the manufacturing of footwear uppers physical, mechanical and hygienic characteristics of leather were also increased. Processing of the footwear upper materials allows to increase operational performance of technical products and extend their lifespan. The following application of the new technology of cutting the modified materials with the processed treated tools that has protective diffusion coating will allow to obtain high quality of the finished leather products at the final stage and decrease the ineffective outage time of the equipment in leather industry.

References

[1] Osin Yu N, Makhotkina L Yu, Abutalipova L N and Abdullin I Sh 1998 SEM and X-ray analysis of surface microstructure of a natural leather processed in a low temperature plasma Vacuum v 51(2) pp 221-225.
[2] Makhotkina L Yu and Sharifullin S N 2016 Design of special purpose products made of nanomodified collagen-containing materials with radio-frequency discharge IOP Conference Series: Materials Science and Engineering v 134, 012020.
[3] Khristoliubova V I, Kashapov N F and Shaekhov M F 2016 Gas and plasma dynamics of RF discharge jet of low pressure in a vacuum chamber with flat electrodes and inside tube, influence of RF discharge on the steel surface parameters IOP Conference Series: Materials Science and Engineering v 134, 012017.
[4] Makhotkina L Y and Khristoliubova V I 2015 Variation of footwear wear resistance depending on methods of treatment. International Journal Of Applied And Fundamental Research № 1, URL: www.science-sd.com/460-24749 (11.03.2015).
[5] Sirazieva L F, Stepin S N and Makhotkina L Yu 2004 Dispersing agents for emulsion type coating compositions (review) Lakokrasochnye materialy i ikh primenenie № 10, pp 25-28.
[6] Makhotkina L Yu 2006 Processing of integrated footwear materials by RF plasma of reduced pressure Leather and footwear industry № 5 pp 36-37.
[7] Ladianov V I, Gilmutdinov F Z, Nikonova R M, Kashapov N F, Shaekhov M F and Khristoliubova V I 2017 Effects of low pressure radio frequency discharge on the physical and mechanical characteristics and chemical composition of diffusion coating on a surface of complex configuration details J. Phys.: Conf. Ser v 789, 012031.
[8] Makhotkina, L Yu and Khristoliubova V I 2017 Studies of the influence of nonequilibrium plasma thermal exposure on the characteristics of the capillary-porous polymer material J. Phys.: Conf. Ser v 789, 012031.
[9] Makhotkina, L Yu, Khristoliubova V I and Khannanova-Fakhruutdinova L.R. 2016 Design of special purpose products made of nanomodified leather Mathematics Education 11(6) iejme.2013.134, pp. 1495-1503.