Investigating the Effect of Plasma Treatment and Amine-Based Surfactants on Quality of Sheepskin Dyeing

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Abstract. The paper presents the results of studying the effect of non-equilibrium low-temperature plasma (LTP) and synthesized non-ionic and cation-active amine-based surfactants on the quality of acid dyeing of wool and leather sides of sheepskins. The plasma treatment conditions, which led to high quality in colour intensity and uniformity of dyeing along both the height of a wool fiber and sheepskin surface area, were determined (U=3.0 kV; I=0.8 A; Wp=2.15 kW; τ=5.0 min; G =0.04 g/s; plasma gas – argon). The study showed that the application of surfactants for the dyeing process led to an increase in dye selectivity ranging from 90% to 100%. A significant increase in dye resistance to dry friction of sheepskins as well as in their strength and elastic characteristics after low temperature plasma treatment was observed (grayscale level was 5; the tensile strength at breaking increased by 10%, the tensile elongation of a leather fabric after dyeing increased by 15%). The study proved the efficiency of the technology which combined plasma treatment and dyeing of sheepskins in the presence of synthesized surfactants used as dye-leveling agents.

1. Introduction
One of the main advantages of low-pressure radio-frequency plasma is that the average electron energy differs significantly from the energy of heavy particles. Moreover, effective formation of various active particles leads to a significant increase in chemical activity of plasma gas subjected to low-pressure plasma [1]. Therefore, the treated surfaces heat up slightly, despite fast heterogeneous processes occur. A few seconds of plasma treatment may be enough to change the surface energy. This allows us to process organic materials, including the materials of animal origin, without causing noticeable destructive processes.

It is known that performance characteristics of semi-finished products, such as colour resistance to dry friction and light resulted from plasma treatment, increase. The combined use of non-equilibrium low-temperature plasma and surfactants intensifies the process of dyeing due to increase in uniformity of colouring by both wool fiber height and sheepskin surface area [2-5].

2. Materials and methods
The aim of this study is to evaluate the uniformity and intensity of acid dyeing of sheepskins after plasma treatment and using amine-based nonionic and cationic surfactants synthesized at the
Department of Plasma Technology and Nanotechnology of High Molecular Weight Materials of Kazan National Research Technological University [6-8].

The objects of the study are semi-finished product samples (sheepskins). Most fur finished products are manufactured from sheepskins using fine-wool, semi-fine-wool and medium wool sheep breeds. Different modern technologies are used to improve the appearance of sheepskins which are sheared, dyed, combed, glossed and subjected to printing and finishing.

The modes of plasma treatment of semi-finished fur products are presented in Table 1.

**Table 1.** Semi-finished sheepskin plasma treatment modes before dyeing.

| Plasma treatment parameters | Plasma treatment modes |
|----------------------------|------------------------|
|                            | 1          | 2          | 3          |
| U, kV                      | 1.5        | 3.0        | 3.0        |
| I, A                       | 0.3        | 0.5        | 0.8        |
| W_p, kW                    | 1.5        | 1.15       | 2.15       |
| τ, min                     | 1.0        | 5.0        | 5.0        |
| G, g/s                     | 0.04       | 0.06       | 0.04       |
| Plasma gas                 | Argon      | Argon      | Argon      |

The dyeing process was followed by retanning and neutralization of the semi-finished sheepskins. The shrinkage temperature of the samples processed in plasma after retanning was 92-95 °C. It was higher than the temperature of the reference sample by 3-50 °C. The process of dyeing followed neutralization immediately. The acid dye Alisarin Wine KA-8 (Lowenstein) was used to dye the sample a burgundy colour. The dye-leveling agent Level P (Lowenstein) was used for control testing.

3. Results

It is known that any object in plasma charges negatively that leads to the formation of electric double layer at its surface. When materials are processed in low pressure radio frequency plasma, the positively charged layer is also created, including a double layer. In the positively charged layer, plasma ions accelerate and bombard the material surface, transferring the energy to the atoms on the sheepskin surface. In addition, a non-self-maintained volume discharge is formed in the pore volume of a sheepskin. As a result, collagen molecules on the inner surface of the pores and capillaries are exposed to the energy. The combined effect of surface and bulk treatment leads to the modification of physical, mechanical and chemical characteristics of wool and leather of a sheepskin.

The quality of dyeing was evaluated by the selectivity of the dye. The selectivity was determined by the change in the optical density of the dye bath, the reflectance spectra of the dyed wool, the resistance to dry friction, as well as by organoleptic evaluation (visual determination and by touch).

The selectivity of dye baths was calculated using the optical densities at the beginning and at the end of dyeing process (Equation 1):

\[ V = \frac{(D_H-D_K)}{D_H} \times 100\% \]  

where \( D_H \) – the optical density at the beginning of the dyeing process; \( D_K \) – the optical density at the end of the dyeing process.

Sampling was performed after adding the dye to the solution to determine the optical density of the dye bath. Then the optical density was determined before dosing each portion of the acid and at the end of the dyeing process. The optical density was measured with a ПЭ-5300ВИ spectrophotometer.
Preliminary plasma treatment was found to have a negligible effect on the measured parameters (by 5 - 7%). However, the depth and uniformity of colour of the samples treated in radio-frequency plasma looked visually better. The best results were obtained using the mode 3 (Table 1). The dependences of the dye bath optical density on the time of dyeing are presented in Figures 1 and 2. It was established that using the synthesized surfactants during the dyeing process leads to a high selectivity of the dye (90 – 100%).

![Figure 1](image1.png)

**Figure 1.** Dependence of optical densities of dye baths on dyeing time (experimental dye-leveling agents).

![Figure 2](image2.png)

**Figure 2.** Dependence of optical densities of dye baths on dyeing time (reference dye-leveling agents).

The colour characteristics of the dyed sheepskins were measured with a X-Rite Color Digital Swatchbook® portable and handheld spectrophotometer using the Lab colour space based on light reflection. The lightness was expressed by the coordinate L. The colour channels were represented by
the rectangular coordinates a and b. The a coordinate indicates the colour from green to red, the b coordinate – from blue to yellow.

Table 2 presents Lab colour space coordinates for the samples dyed in the presence of synthesized amine-based non-ionic and cation-active surfactants. The parameter dE characterizes the discrepancy in the colour intensity of the reference and experimental samples and it is a criterion for the accuracy of colour reproduction. In saturated colours, the dE value is sufficient for adequate colour reproduction.

Table 2. Colour characteristics for sheepskins

| Measured object | Treatment before dyeing                        | L     | a     | b     | dE  |
|-----------------|------------------------------------------------|-------|-------|-------|-----|
| Sheepskin       | Without using low-temperature plasma          | 26.46 | 29.58 | 1.93  |     |
|                 | Using low-temperature plasma                  | 24.64 | 27.48 | 0.24  | 3.25|

The results obtained by transmitting the spectrophotometer readings through the X-Rite Color Digital Swatchbook software are shown in Figure 3.

Figure 3. Reflection spectra of wool side of a sheepskin dyed a burgundy colour.

Reflection coefficients change to a greater extent in the red and blue regions of the spectrum. Test samples are characterized by low reflection coefficients resulting from high colour intensity of wool side over the surface area of sheepskins. These measurements were carried out in 5 different topographic sections of the sheepskin surface.

The obtained results can be explained by the fact that low-pressure radio-frequency plasma treatment causes opening of plates of wool fiber flakes due to the transfer of negative charge to the cuticle keratin. This leads to mutual electrostatic repulsion of the same cuticle flakes from each other and
their opening. Dye molecules diffuse more easily into the cortex and core of a wool fiber. The addition of non-ionic surfactants at the beginning of the dyeing process promotes both the external diffusion of the dye from the solution to the surface to be coloured and the internal diffusion of molecules of dye to the reactive sites of protein, while cation-active surfactants increase the adsorption of dye and its binding to wool fibers. It was proved that low-pressure radio-frequency plasma treatment of sheepskins leads to the increase in dye resistance to dry friction. During the dyeing process, the acquired negative charge almost disappears from the surface of cuticle flakes. The electrostatic forces of mutual repulsion decrease. The cuticle flakes gradually return to their original position and the flakes “close”. Regardless of low-temperature plasma modes, the experimental samples subjected to low-temperature plasma treatment showed a high resistance to dry friction (gray scale level was 5), while the samples which were not treated by plasma had lower values of resistance (gray scale level ranged from 4 to 5). Processing of semi-finished sheepskins allowed us to produce dyed fur product with increased elastic and strength characteristics: the tensile strength at breaking increased by 10% on average, the tensile elongation increased by 15% (Table 3).

**Table 3.** Characteristics of semi-finished sheepskins after low-temperature plasma treatment and without plasma treatment

| Characteristics | Values | GOST 4661-76 requirements | No low-temperature plasma treatment | After low-temperature plasma treatment |
|-----------------|--------|--------------------------|-------------------------------------|----------------------------------------|
| **For leather of sheepskins** | | | |
| Moisture content, % | Not greater than 14.0 | 12.0 | 12.1 |
| Shrinkage temperature, °C | Not less than 70 | 88.0 | 93.0 |
| The pH-value of aqueous extract | 4.0-7.5 | 4.5 | 4.6 |
| Ash content, % | Not greater than 10.0 | 8.4 | 8.6 |
| Weight content of unconnected greasy substances, % | 10.0-20.0 | 16.0 | 15.8 |
| Tensile strength, MPa | Not less than 9.8 | 11.2 | 13.2 |
| Total elongation at strength 10 MPa, % | Not less than 30.0 | 33.0 | 38.8 |
| **For wool side of sheepskins** | | | |
| Weight content of unconnected greasy substances, % | Not greater than 2.0 | 1.6 | 1.5 |
| Resistance of dyed surface to dry friction (according to levels of gray scale) | Not less than 3 | 4-5 | 5 |
| Colouring light resistance of wool of sheepskins (according to levels of gray scale) | 4 | 4-5 | 5 |

**4. Conclusion**

Thus, it has been concluded that plasma treatment of sheepskins improves its performance characteristics: the dye resistance to dry friction and strength characteristics. The co-use of low-
temperature plasma and synthesized surfactants intensifies the dyeing process by increasing the uniformity and saturation of the colour along by both wool fiber height and surface area of sheepskins.

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