The influence of the capacitive coupled radio-frequency discharge on cotton fiber and technological effects of its application

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Abstract. The authors studied the effect of capacitively coupled radio-frequency (RF) discharge at low pressure on cotton fiber. It is shown that non-cellulose impurities of cotton fiber are removed during processing: the content of extracted substances is reduced by 22-70% depending on the type of solvent when using air, by 5-6% – when using argon. The surface of the fibers becomes hydrophilic, additional submicroscopic pores appear, the roughness increases 1.6 times, water absorption increases 1.5-1.8 times. Discontinuous knitted fabric dyeing was carried out varying the concentration of the active dyes (remasol) in the dye-bath. It was found that the sorption capacity of cotton fibers in relation to the dye increases on average 1.1-1.25 times. To achieve the required color intensity of plasma pre-treated samples dye concentration on average 10-30% less than in the controlled dyeing is needed. The concentrations of dyes that allow obtaining the same intensity of color for the knitted fabric prepared in different ways are selected.

1. Introduction

Non-equilibrium low-temperature plasma is a universal tool that allows changing the properties of different materials, such as textiles, depending on the type of plasma gas and processing parameters. The main processes in charge of technological effects from the textile materials processing of with non-polymerizing gases are etching of the fiber surface and changing of the functional group compositions. With optimal plasma treatment parameters, these processes lead to the cleaning and activation of the material, which allows the liquid-phase finishing operations intensification [1-3].

Cotton fiber is a «tube» filled with cellulose that is placed inside in layers (growth rings) and covered with a thin monolithic fat-wax layer. In addition, paraffin is applied to the threads before knitting to reduce tears and facilitate knitting. For further processing, paraffin should be removed from the surface of the knit. These layers determine the moisture, physical, mechanical and optical properties of the fiber and performs a protective part [4]. At the same time, it prevents the penetration of finishing reagents during cotton processing. In addition, before the process of obtaining textile material (weaving or knitting) cotton yarns are treated with excipients (dressing, paraffin composition). They are further removed before the dyeing process. The authors consider plasma treatment in non-polymerizing gases as an alternative to traditional liquid processes of cotton textile materials preparation for dyeing (on the example of knitted fabric).
2. Research objects and methods
The objects of the study were grey (nontreated) paraffined cotton yarn and grey (immediately after knitting) knitted fabric. Sample processing was conducted in capacitively coupled RF discharge at low pressure. Its advantage in comparison with other gas discharges is that the discharge is ignited both at the surface in contact with the flow of the plasma-forming gas and in the pores and capillaries of fibrous materials that do not have direct contact with the plasma [5]. This is due to the electrons oscillations in the RF electric field: the boundary of the positive charge sheath (PCS) oscillates with the frequency of the field, resulting in the negative potential of the sample surface during the period changes. The boundaries of the PCS and, accordingly, the potentials of the opposite sample sides change in counterphase with each other. As a result, an electric potential difference occurs between the opposite specimen surfaces. Correspondingly, an alternating electric field arises into cotton material, that polarizes cellulose and non-cellulose molecules. As consequence, the electrical breakdown between the opposite walls of the capillaries are created, this causes changes on the inner surface of the fibrous-porous material and seems like volume treatment [5].

Processing of samples was carried out on the installation supporting the following plasma parameters of capacitively RF discharge: \( P = 13.3 \) Pa, the degree of ionization is in range of \( 10^6 – 10^4 \), the concentration of charged particles \( n = 10^{15} – 10^{17} \) m\(^{-3}\), gas temperature is in range of \( 60 – 90^\circ \)C, the density of ion current to the surface of the sample \( j_i = 0.3 – 1.0 \) A/m\(^2\), the energy of ions arriving at the surface of the sample \( W_i = 70 – 100 \) eV [5]. Plasma gases were air and argon in the proportion of 7:3. Before and after plasma treatment the surface of cotton fibers was studied by electron microscopy scanning using the workstation «AURIGA CrossBeam» («Carl Zeiss NTS», Germany) in the mode of detection of secondary electrons; also the method of atomic force microscopy with the device «NT-MDT NTEGRA» («NT-MDT», Russia) was used. The change in the fiber surface composition was recorded by secondary ion mass spectrometry (SIMS) method on the device «TOF-SIMS 5» («ION-TOF», Germany). The viscosity of copper-ammonia solutions of cotton fiber cellulose was determined by a standard method [6], the content of fat-wax and paraffin substances was determined by extraction with organic solvents (isopropyl alcohol, carbon tetrachloride, and diethyl ether) [6]. The finishing of samples, exactly the dyeing process, was carried out in the laboratory according to standard methods [3]. The concentration of dye solution \( C \) varied from 0.5 % to 7% by weight of the fabric, then determined the coloristic parameters. The most popular active dyes remazols were used for cloth dyeing. The color intensity was determined by the Gurevich-Kubelka-Munk \( K/S \) function [6].

3. Results and discussion
The content of substances extracted by organic solvents in the samples is reduced by 22-70% (depending on the type of solvent) after plasma treatment in the air; when processed in argon and air mix, it decreases by 5-6%. These results indicate the removal of paraffin and fat-wax substances from the surface of the cotton fiber, that means its cleaning from non-cellulose impurities. At the same time, the plasma does not significantly affect the cellulose part of the fiber: the viscosity of copper-ammonia solutions decreases slightly (by no more than 5%). Due to the removal of non-cellulose impurities from the fiber surface its microrelief changes; the etched areas 10–20 nm in size appear, the average \( R_a \) roughness increases 1.6 times. The SIMS method showed a change in the fiber surface composition: the number of ions corresponding to oxidized hydrocarbons \( \text{C}_{17}\text{H}_{32}\text{O}_2^+ \), \( \text{C}_{18}\text{H}_{36}\text{O}_2^+ \), \( \text{C}_{19}\text{H}_{38}\text{O}_2^+ \), increases dramatically 20 – 50 times, and the number of nitrogen-containing ions also increases. At the same time, there is a change in the macro parameters of the samples after treatment in the RF capacitive discharge plasma: the height of water rise along the vertical capillaries increases greatly, the water absorption increases 1.5 – 1.8 times. Moreover, the change in hygroscopic indices in the air plasma is more pronounced.
All the above changes in cotton fiber (removal of non-cellulose impurities, hydrophilization of the surface, an appearance of additional submicroscopic pores) contribute to the increase in its sorption capacity. Therefore, at the next stage of work, experimental dyeing of the knitted fabric was carried out.

It is revealed that plasma treatment does not affect the dyeing uniformity. This indicates the ability of the RF discharge plasma to uniformly change the surface properties of the material. The resulting colorings are resistant to operational effects, which is provided by a high degree of binding of the dye to the fiber. Plasma treatment allows increasing the amount of bound dye on average 1.1-1.25 times. Photographs of sections of the colored fabric (figure 1) indicate that it is evenly dyed over the thickness. Consequently, the plasma affects the fibres located in the depth of the material, which once again confirms the effect of the volume processing of the knitted fabric by the RF discharge plasma.

![Photograph showing the cut of dyed knitted fabric](image)

**a** - prepared for dyeing according to standard technology  
**b** - prepared for dyeing by plasma treatment

The practical interest was in studying the potential of low-pressure RF discharge to solve the problem of reducing the dyes consumption and obtaining uniform stable colors, similar to the color of reference samples.

It is necessary to obtain the dependences of the \( K/S \) staining intensity by the dye concentration and the dyeing time \( t_k \) for the reliable description of the obtained dependencies. For this purpose, experimental data were approximated using a logistic curve (Pearl-Reed model)

\[
f(K/S) = \frac{a_0}{1 + a_1 \exp (-a_2 t_k)} = y(t_k),
\]

where \( a_0, a_1, a_2 \) are the coefficients obtained using MS Excel program which converted (1) to the following equation:

\[
\frac{a_0}{y(t_k)} = 1 + a_1 \exp (-a_2 t_k)
\]

(2)

All obtained curves reliably describe this dependence

\[
\left( \sum_i \Delta x_i^2 \right)^{1/2} \left( \sum_i x_i^2 \right)^{-1/2} \leq 0.05.
\]

(3)

Experimental dyeing has shown that the required color intensity of knitted fabrics pretreated with plasma is achieved when the dye concentration is on average 10-30% lower than the control ones. For example, in the case of dyeing the fabric with remazol «Marengo RR» (figure 2) the sample prepared only by plasma treatment with \( C = 3\% \) corresponds to \( K/S \) is similar to the sample prepared by boiling at \( C = 3.75\% \). That means that, in this case, it is possible to reduce the dye consumption in the dye-bath by 25%.

Based on these data, we are able to select the concentration \( C \) of dyes allowing to obtain the same color intensity for fabric prepared in different ways. The coefficients of color difference \( \Delta E \) were
calculated, the reference samples were dyed according to the typical technology (with preparation by boiling or bleaching).

**Figure 2.** The intensity of K/S dyeing of a cotton knitted fabric prepared by different methods depending on the dye concentration $C$ (active remazol «Marengo RR», $t_c = 60$ min)

4. Conclusion
The low-pressure RF discharge affects only a thin near-surface layer of cotton fiber, retaining its main cellulose component. Plasma treatment is a gentler method of processing the fabric in comparison to traditional processes of preparing for dyeing. Plasma treatment (in treated gases) leads to the hydrophilization of the fiber surface, the appearance of additional submicroscopic pores and contributes to increasing the fiber sorption capacity. At dyeing plasma-treated samples, it is required dye on average by 10-30% less than for control samples.

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