COMPOSITION FOR FINAL FINISHING FABRICS FROM NATURAL SILK 
BASED ON HYDROLYSIS PRODUCT OF POLYACRYLONITRLE COPOLYMER

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Abstract
This paper focus on composition for final finishing fabrics from natural silk based on Hydrolysis product of Polyacrylonitrie Copolymer. It incudes different experiments and literature from previous studies is also used. On the bsis of results , at the end discussion and conclusions are drawn.

Keywords: COMPOSITION ; FINISHING ; FABRICS ; NATURAL SILK ; HYDROLYSIS ; POLYACRYLONITRLE COPOLYMER

1. Introduction

Growing demand for silk fabrics and in creasing the their assortment due to producing costume and shirt fabrics manufactured on the base of natural silk requires working out, new methods of finishing which can provide high operational qualitative properties.

Silk fabrics that have good hygienic properties, natural luster and good quality can shunk and crease .Having good hygienic properties, natural luster and wearing efficiency silk fabrics shrink and crease. At the present time for adding the properties of little creasing and little shrinking for the fabric from natural fibers dimetilolcarbamide and its derivatives are practically applied. Wide application of pre-condensates of thermoactiveetting resins is caused by high effects of wrinkle resistance and little shrinkage attained after finishing, however, due to fixation of fiber structure and increasing its stiffness visible deterioration of materials mechanical properties takes place, its breaking load decreases. In different years, to add shape stability to fabrics made of natural silk [1] the compositions based on formaldehyde-containing preparations were offered.

How increasing its stiffness visible takes place its The main disadvantage of such preparation is containing free formaldehyde on the finished textile materials.

Fibroin of natural silk belongs to relatively stiff chained polymers, to decrease deformation putting resinous substance in to amorphous structure of natural silk causes increasing of the fabric stiffness and loss of silk fabrics original softness and elasticity.

A radical method for improving hygienic properties of fabric with little shrinking and little creasing finishing is using biofunctional compounds on the base of nonformaldehyde and little formaldegidnyh compounds [2-9]. In industrial conditions only some of them are used, moreover, the applied methods are not always ecologically expedient and when using polycarboxylic acids the color depth of the samples dyed with acid and direct dyes, decreases.

Researching possible use of “K-4” preparation in final finishing of silk fabrics, is of great scientific and practical interest. The product of alkaline polyacrylonitrile (PAN) hydrolysis is a viscous, sticky film-forming system. The film on the base the saponificated polyacrylonitrile has the strength of 5.2-5.9 kg/mm² lengthening 160-200%, and 3.0-4.0 times exceeds water absorption of the film made of from polyvinyl alcohol (PVA) [10]. In addition, availability in the chain of “K-4” macromolecules of carboxylate and amide polar groups (-OH, -NH₂, etc.) in amino acid remainsof fibroin does not exclude the possibility for forming chemical ties between natural silk and finishing composition on the base of “K-4”.

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EXPERIMENTS
The use of “K-4” preparation as a binding one in finishing composition was determined due to its properties, such as, adhesiveness, film formation and availability of functional groups, actively coming in the chemical reaction at high temperature in catalyst availability.

Water-soluble “K-4” preparation was obtained by the PAN hydrolysis in aqueous solution of alkaline agent when heated to 96-100 °C for 4-5 hours, it is produced in a Navoiazot Industrial Association. (TU Uz.6.1-53-95). The composition of product PAN saponification with sodium hydroxide is as follows:

\[-(C_2H_2COONa): (C_2H_2CONH_2): (C_2H_2CN) = 63% : 34% : 3%\]

As the hydrolyzed product of PAN copolymer “K-4” preparation was used for final finishing for the first time, researching work for determining the composition was carried out.

As a film-forming, PVA and ammonium chloride, sodium phosphate and potassium catalysts were tested. To realize the assumed chemical reactions of “K-4” preparations with fidroin silks the alkaline medium was required, thus, the effect of pH finishing medium on the quality of a finished fabric was researched and the limit of finishing composition alkalinity was determined.

In the result of the researching work composition structure of finishing mixture defined containing the following component in was g/l: K-4 preparation 20±70; PVA –10±35; NaH_2PO_4 catalyst - 10, pH 8.5 ± 10.5 and technological sequence. The finishing silk fabric with finishing mixture was carried out in the following sequence:

- Soaking (at 60°C; τ = 0.5 min) → wringing out (to the degree of 90 ± 1%) → drying (at 105±2°C; τ = 5 min) → heat treatment (at 140±2°C τ = 8 min).

The fabric from natural silk "crepe de Chine" was chosen for the research. It has, has "Crape" interlacing of natural silk yarn with linear density 2.3 tex x 4 yarns, twist 2000 tw/m.

For comparing the effect of the proposed finishing composition on the quality of fabric finishing mixture on the basis of dimetilolcarbamide - “Karbamol SEM” with the following composition of components in g/: “Karbamol SEM” 100, PVA-25; NH_4CI-20 was used.

Qualitative indicators of original and finished fabric were researched in the accredited studying-certification center “CENTEXUZ”, in TITLI using the following devices: AUTOGRAPH AG-1, Monsans-AW, “AR-360SM”; microscope “Nikon”, PT-2, AR-360SM “Frazie.tye Air Permeabiliti Tester”; fabrics stiffness was determined by the method of the Consoly on PT-2; flexometre

The effect of final finishing on the functional quality of “crepe de Chine” fabric is given in Table 1.

When finishing the fabric with the composition containing «Karbamol SEM”, the total opening angle (TOA) increases. At the same time the finishing increases fabric stiffness decreases capillarity and make sworse the appearance of the fabric.

With increasing the concentration of the “K-4” preparation the TOA values increase to 11-48 degrees, additional weight is 9-12.5%, decreasing shrinkage - in 2.5 times. The finishing process has no negative effect on the stiffness, of the fabric and elasticity and crape effect of the fabric remaine, at the sometime, capillarity is improved. Microscopic researching of the surface of original and finished fabric have shown that warp and weft yarns in finished samples are compressed by covering their surface with the polymer film. As a result, due to the yarns compression inter yarns space increases and causes increasing in capillarity in 1.3 -2.0 times and air permeability in 1.7 times.

Concentration increasing of “K-4” preparation in finishing composition doesn’t considerably increase additional weight and quality of finishing. Its increasing to 100 g/l causes decreasing in physical
and mechanical properties of finished fabric (Table 1).

Best quality indicators of finished fabric were obtained at a concentration of the “K-4” preparation = 40±50 g/l. Further researches were carried out at this concentration. The role of each component of finishing mixture for the quality of finishing, effect of the composition structure with alternate removing the components from finishing mixture were researched. Table 2 shows the results of the experiment.

As it is evident from the data, the lack of “K-4” preparation in finishing mixture, causes a film forming on the fabric surface, with additional weight of 13.5%, however, the washing out ability of appreta has high values. A similar phenomenon was observed in the lack of a catalyst.

The lack of PVA in the composition of finishing mixture reduces the formation of additional weight, the washing ability out of such film remains high. Qualitative indicators of the finished fabric, such as total opening angle, shrinkage get much worse. The medium of finishing composition has pH = 8 ± 0.5, as increasing alkalinity is necessary to create favorable conditions for interaction natural silk (NS) with components finishing mixture.

Without additional increasing medium alkalinity, the quality of finishing is improving, but the strength is reduced and simultaneously the rigidity of fabric increases (Table 2). The results of the experiment show that in the case of using “K-4” preparation in the finishing composition the latter plays a binding and film-forming role. Film forming on the surface of the fabric by the composition containing only the “K-4” preparation is not enough to improve the quality of silk fabric.

Improvement the quality characteristics of NS fabric by the effect of composition containing the “K-4” preparation and the low washing off finishing mixture allows us to suggest that with filling the pores and film formation on the surface of fibers, the preparation chemically interacts with fibroin silk (FS). This is facilitated by the presence of a catalyst in finishing mixture, high-temperature processing and alkaline medium.

To confirm the chemical interaction components of finishing mixture and FS the amount of bound polymer was determined by the dissolution method. The mixing solvents NaCNS: CH₃COOH was used in the ratio of 75:25 (volume). In the mixing solvents at 25 ° NS [11] as well as K-4 preparation and PVA is dissolved. 1% solution of appreta fabric was made. Dissolving was made at in door temperature. The solution was filtered through a Shota № 3 filter. Polymer precipitate was washed in the following sequence: acetone → water → acetone, for complete removing solvent and water.

The influence of PVA and “K-4” concentration on the amount of bound polymer as a result of the finishing touches by the proposed composition was researched.
The increase in PVA in finishing mixture in range of 10 ÷ 35 g/l causes increasing the number of cross-linked molecules of fibroin, however, the stiffness of fabric significantly increases (Fig. 1). The dependence of the cross-linked polymer amount on “K-4” concentration passes through its maximum when 40-50 g/l of polymer is contained in finishing mixture.

The results of the research show that in final finishing, the transversal linkage of FS macromolecules takes place, it improves its quality characteristics. The number of cross-linked macromolecules in the selected technological regime was 0.29%.

Sorption properties of finished fabric and film of finishing mixture (Fig. 2) were determined by the sorption of water vapor and were researched, with the help of spring tungsten Mak - Ben balance with sensitivity of 1.5 mg / mm at 25 +0.1 °C and the residual pressure of 10.5 mm. mc. 5 parallel definitions were made. Relative error of measurement was 1.5%. The estimate of pore radius, Å, was made according to the method [12].

According to sorption isotherms specific surface area – $S_s$ of silk. $S_s$ of silk was calculated by the equation of Brunauer - Emmett - Teller (BET) according to the method.

The total pore volume is calculated by the formula:

$$W_0 = \frac{a}{\rho}$$

where

$a$ – the weight of adsorbent, taken at saturation $P/P_0=1$
Table 1

The influence of finishing composition on the quality of “crepe de Chine” fabric finishing

<table>
<thead>
<tr>
<th>№</th>
<th>Structure of finishing mixture composition, g/l</th>
<th>Additional weight, %</th>
<th>Washing out of finishing mixture, %</th>
<th>TOA, degree</th>
<th>Stiffness of fabric, мкН. см²</th>
<th>Capillarity mm/min</th>
<th>Breaking strength, N</th>
<th>Breaking lengthening %</th>
<th>Shrinkage, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Original fabric</td>
<td>-</td>
<td>-</td>
<td>223.0</td>
<td>1.05</td>
<td>40</td>
<td>404.6</td>
<td>18.8</td>
<td>8.7</td>
</tr>
<tr>
<td>2</td>
<td>«Karbamol SEM”-100 PVA-25 NH₄Cl-20</td>
<td>12.30</td>
<td>1.05</td>
<td>255.0</td>
<td>1.63</td>
<td>34</td>
<td>387</td>
<td>19</td>
<td>3.4</td>
</tr>
<tr>
<td>3</td>
<td>K-4 – 20 PVA-25 NaH₂PO₄-10 pH = 10</td>
<td>9.20</td>
<td>1.71</td>
<td>234.0</td>
<td>1.14</td>
<td>52</td>
<td>384</td>
<td>22</td>
<td>4.5</td>
</tr>
<tr>
<td>4</td>
<td>K-4 – 30</td>
<td>9.60</td>
<td>1.20</td>
<td>241.0</td>
<td>1.10</td>
<td>57</td>
<td>368</td>
<td>18</td>
<td>4.3</td>
</tr>
<tr>
<td>5</td>
<td>K-4 – 40</td>
<td>11.60</td>
<td>0.83</td>
<td>266.0</td>
<td>1.03</td>
<td>71</td>
<td>372</td>
<td>21</td>
<td>3.5</td>
</tr>
<tr>
<td>6</td>
<td>K-4 – 50</td>
<td>12.50</td>
<td>0.68</td>
<td>272</td>
<td>0.98</td>
<td>78</td>
<td>394</td>
<td>22</td>
<td>3.5</td>
</tr>
<tr>
<td>7</td>
<td>K-4 – 70</td>
<td>13.30</td>
<td>0.92</td>
<td>247.0</td>
<td>0.94</td>
<td>74</td>
<td>426</td>
<td>26</td>
<td>4.2</td>
</tr>
<tr>
<td>8</td>
<td>K-4 – 100</td>
<td>13.70</td>
<td>1.10</td>
<td>239.0</td>
<td>0.89</td>
<td>69</td>
<td>376</td>
<td>19</td>
<td>4.4</td>
</tr>
</tbody>
</table>
The influence of finishing composition components on the quality of finished fabric

<table>
<thead>
<tr>
<th>№</th>
<th>Structure of finishing mixture composition, g/l</th>
<th>Additional weight, %</th>
<th>Washing out of finishing mixture, %</th>
<th>TOA, degree</th>
<th>Stiffness of fabric, mN·sm²</th>
<th>Air permeability, sm³/sec·sm²</th>
<th>Breaking strength, N</th>
<th>Breaking lengthening %</th>
<th>Shrinkage, %</th>
<th>warp</th>
<th>weft</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Original fabric -“crepe de Chine”</td>
<td>-</td>
<td>-</td>
<td>223</td>
<td>1.05</td>
<td>100.8</td>
<td>404.6</td>
<td>19.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>“K-4” -50 NaH₂PO₄·10 PVA·25 NaOH pH=10</td>
<td>12.5</td>
<td>0.68</td>
<td>272</td>
<td>0.98</td>
<td>126.7</td>
<td>394.0</td>
<td>22.0</td>
<td>3.5</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>- NaH₂PO₄·10 PVA·25 NaOH pH=10</td>
<td>13.5</td>
<td>4.2</td>
<td>282</td>
<td>0.91</td>
<td>122.9</td>
<td>382.9</td>
<td>25.6</td>
<td>6.3</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>“K-4” -50 - PVA·25 NaOH pH=10</td>
<td>10.0</td>
<td>4.7</td>
<td>271</td>
<td>0.89</td>
<td>122.9</td>
<td>387.5</td>
<td>25.8</td>
<td>5.2</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>“K-4” -50 NaH₂PO₄·10 - NaOH pH=10</td>
<td>7.3</td>
<td>3.8</td>
<td>258</td>
<td>0.82</td>
<td>112.4</td>
<td>404.1</td>
<td>26.7</td>
<td>6.8</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>“K-4” -50 NaH₂PO₄·10 PVA·25 -</td>
<td>12.2</td>
<td>2</td>
<td>264</td>
<td>1.07</td>
<td>120.6</td>
<td>339</td>
<td>20.3</td>
<td>2</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>
\( \rho \) - density of the adsorbent

The average radius of the capillaries is calculated from the ratio

\[ r_n = 2 \cdot W_0 \cdot 10^{-4}/S_{yd} \] [12].

The measurement of sorption capacity indicates that in general there is a tendency of decreasing in sorption capacity of samples of finished fabric. However, the decrease in sorption properties is insignificant compared with the original fabric. Sorption isotherm of the film obtained from finishing composition has significant difference from the original and finished fabric.

\[ \text{Fig.2. Sorption isotherms of water vapor at } 25 \pm 0.1 ^\circ C \text{ of samples 1 - original, 2 – finished, 3 – film of finishing mixture} \]

The final finishing of fabric samples with suggested finishing mixture modifies the surface, capillary and sorption properties. Apparently, the film finishing mixture, which covers the microstructure of fabric surface fills the pores of the fiber. Thus, \( S_{yg} \) decreases. However, larger pores remain not blocked and therefore \( W_0 \) increases (Table 3).

Table 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Original “Crepe de Chine” fabric</th>
<th>Finished fabric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity of the monolayer, ( x_{m, \ r/g} )</td>
<td>0.0158</td>
<td>0.0128</td>
</tr>
<tr>
<td>Specific surface area of pores ( S_{k, m^2/g} )</td>
<td>55.537</td>
<td>45.005</td>
</tr>
<tr>
<td>Total pore volume ( W_0, \text{sm}^3/g )</td>
<td>0.077</td>
<td>0.085</td>
</tr>
<tr>
<td>Average pore radius ( R_k, \text{Å} )</td>
<td>27.7</td>
<td>37.7</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

To give the properties of little shrinkage and wrinkle resistance to fibrous fabric bi-or poly-functioning substances with heightened chemical activity are used. Having been included in the fiber, they will react with the active groups of macromolecules in fibrous fabric blocking them, or forming cross-links between adjacent macromolecules.

Based on the number of cross-links formed between adjacent macromolecules in finishing, the consumption of pre-condensate must be very small. In practice, good indicators of fabric finishing can
be achieved in the case of a large excess of pre-condensates. Their concentration in impregnating solution was 100-250 g/l, considering technical products. Using pre-condensates of synthetic resins in finishing textile fabrics in order to add them the required effect simultaneously causes deterioration of their operational properties and most of the traditional finishing by resin-containing preparations, the content of free formaldehyde of finished fabric exceeds the standards and is up to 0.25-0.3 %.

So to keep natural properties in good made of natural silk, the use of traditionally applied pre-condensates for finishing natural silk has its limitations.

Working out effective method and composition for finishing natural silk fabric in order to improve their operational properties using little- and non-formaldehyde compounds, decreasing prime cost of production the point of view for ecology is also an important problem. Choosing “K-4” preparation as a component of finishing composition was based on its properties. Stickiness-adhesiveness nature of “K-4” preparation was shown by the appearance of hydrogen bonds among molecules as substance with a well-developed ability to form hydrogen bonds with fibroin. In addition, violiarlity of functional groups in “K-4” macromolecule, carboxylated and amide groups does not exclude the possibility for forming chemical link with fibroin. It is assumed to get chemical interaction between “K-4” carboxyl groups with - OH group of fibroin forming ester bond and end amide groups of fibroin forming polypeptide bond. Low washing out of finishing mixture, changes in the total corner of disclosing, physical and mechanical properties indicate the strength of the film finishing mixture on the fabric surface and crepe effect fabric are kept.

In the result of final finishing by the composition sorption properties of finished fabric change slightly.

CONCLUSION
- The proposed composition based of “K-4” preparation can be used for finishing natural silk fabrics, instead of formaldehyde-containing pre-condensates of thermoactive resins.
- The composition gives natural silk fabrics stability and little shrinkage properties in this case elasticity, crepe effect of fabric, its natural properties can be kept.
- The role of each component of the proposed finishing mixture is determined.
- Analytical method shows that the finishing of silk fabric by the proposed composition was carried out when components of finishing mixture chemically interacted with FS.
- In the a result of the finishing touches the macrostructure of NS changes, but the sharp decrease in sorption properties of silk fabric were not observed.
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