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Development of a Polymeric Composition for Antimicrobial Finish of Cotton Fabrics

Abstract
This article considers the development of a new polymeric composition on the basis of polyvinyl pyrrolidone, silver ion solution and benzoic acid for the antimicrobial finishing of cotton fabrics. The advantages of the application of a new composition on the basis of polyvinyl pyrrolidone, silver ion solution and benzoic acid include the availability of the material's use, as well as the simplicity of the technological process: finishing may be performed with any tenter drier aggregated with a padding machine and combining the drying process and thermal treatment. The newly developed efficient composite formulation for biocidal finishing of cotton fabrics is comparatively inexpensive, environmentally safe, and resistant to wet treatment. Its application offers opportunities of manufacturing of a wide range of competitive, environmentally compatible, and biologically stable cellulose textiles with various textures and various fabric weights. As a result of the study it has been found out that cotton fabrics finished with the composition on the basis of polyvinyl pyrrolidone, silver ion solution and benzoic acid have advanced antimicrobial characteristics preventing fouling with mould fungi and are not deteriorated by microorganisms under operational conditions.

Key words: *cotton fabrics, antimicrobial finish, polymeric composition, polyvinyl pyrrolidone, silver ion.*

Introduction

Conditions of cellulose textile manufacturing and operation presuppose contact with microorganisms, therefore there is a risk of textile biological deterioration. Microorganism activity can result in the deterioration of the appearance of products, spotting, odour issues, strength reduction and finally in loss of aesthetic characteristics and performance properties. According to the data published above, 40% of total losses of textile in the course of processing, storage and operation is due to biological deterioration. An Increase in the resistance of textiles to such effects will not only extend the service life of fabrics but make them practically indispensable for specific operating conditions.

Finishing, the process of coating textile with various high-molecular compounds in the form of solutions, emulsions or latexes, is one of the most radical ways to achieve these objectives.

However, the problem of the production of textiles with antimicrobial characteristics with the retention of their natural properties by means of accessible and environmentally compatible technologies is not completely solved yet.

Besides, the well-known technologies of biocidal finishing do not always meet the basic requirements for antimicrobial polymeric coatings, such irritant effect on human skin, as well as retention of antibacterial properties of the products over the longest possible useful life period under the conditions of repeated washing [1 - 6].

In this context, the objective of research involved search for a technology of biologically protective finishing the cotton fabrics by means of the substances safe for human's health, able to form chemical bonds between each other and with cellulose of fibres.

Research subjects and methods

Research subjects

The subject of the research carried out within this work was cotton fabric of the coarse calico group, article number 03S7-BCH484.

Structural characterisation of the cotton fabric is shown in ***Table 1***.

Table 1. *Structural characteristics of cotton fabric.*

Fabric width, cm	150 ± 2
Fabric weight, g/m^2	142 ± 7
Number of fibres in 10 cm warp weft	 261 ± 5 229 ± 7
Breaking load of strip 50×200 mm, N warp weft	 32 37
Weave	Plain
Fabric dimensions measured after wet treatment, % warp weft	 5.0 2.0

Basic substances

Polyvinyl pyrrolidone (PVP) – is a white coloured amorphous polymer with a linear structure; its molecular weight ranges from a few hundred to several hundred thousand depending on the conditions of preparation; it is easily soluble in water and in most organic solvents, and is insoluble in ether, aliphatic and alicyclic hydrocarbons. Polyvinyl pyrrolidone is compatible with many synthetic and natural resins as well as plasticising agents.

Silver (Ag) – is a white metal remaining almost unchanged when exposed to air at room temperature; however, because of the presence of hydrogen sulfide in the air in the course of time it becomes covered with a dark silver sulphide coating. The bactericidal properties of silver have been known since ancient times. As a result of the study of silver bactericidal properties it has been found that a crucial role is played by positively charged silver ions Ag^+. The intensity of silver ionisation increases in aqueous solutions. Silver cations inhibit the activity of the enzyme, which provides oxygen exchange in the simplest microorganisms: pathogenic bacteria, viruses and fungi (about 700 species of pathogenic "flora" and "fauna").

Benzoic acid (BA) – is an organic compound containing the carboxyl group (COOH). The hydroxyl group in the carboxyl causes its acidic nature. Benzoic acid is a crystalline substance with a pungent odour, soluble in water.

Experiment procedure

Prior to the experiment, unfinished bleached cotton fabric was washed in distilled water in order to remove residues of the bleaching bath. In order to accurately determine the weight, the sample was conditioned in an exiccator over dehydrated $CaCl_2$ after drying.

Upon determination of the true weight with the help of an analytical balance, the sample of cotton fabric with dimensions of 200 × 200 mm was impregnated with an aqueous solution of polymer composition in a laboratory twin-shaft padding machine with 90% extraction, and drying and heat treatment was performed on a spiked frame in an oven with a temperature controller. Heat treatment was carried out at 145 °C for 2 minutes. After drying and heat treatment the sample was washed with distilled water and then dried at room temperature [7 - 8].

Research methods

Antimicrobial characteristics of the cotton fabrics were checked by means of a microbiological resistance laboratory test (GOST 9.060–75). The method consists in prolonged exposure of finished or original fabric samples to a natural soil microflora complex by applying it on the surface of the fabric under certain conditions, and in consequent determination of its resistance to microbial destruction (P). According to GOST 9.060–75, a fibre shall be considered resistant to microbiological deterioration when $P \geq 80\%$.

The microbiological deterioration resistance factor (P) in percents is calculated by the formula:

$$P = B_T \times 100 / B_R \qquad (1)$$

where B_T – is the breaking load of the strip tested in g; B_R – is the breaking load of the reference strip in g.

Microbiological studies were also conducted according to GOST 9.048-89. The method consists in the infection of decontaminated samples with water suspension of fungal spores (*Aspergillus niger, Pennicillium brevi and Trichoderma viride* according to GOST 9.802 – 84), which are then kept in conditions optimal for their incubation over 28 days.

A strip-breaking machine - RT-250M was used to determine the characteristics by the strip-method (GOST 3813-72).

Air permeability was determined by means of a VPTM-2 instrument according to GOST 12088-77.

Air permeability in $dm^3/m^2 \times sec$ for each point sample is calculated by the formula:

$$Q = (V_{av} \times 10000)/S, \qquad (2)$$

where V_{av} – is the average air consumption for one point sample in dm^3/sec; S – is the finished area in cm^2.

Interaction of the composition with the cellulose macromolecule was studied using an IR-spectrograph.

The surface and structure of the finished samples was examined by scanning electron microscope - JSM-6490LA, made in Japan.

Software packages (PPP) STATISTICA 6.0 and Excel were used to determine optimal conditions of the technological process.

Results

Studies on the use of polyvinyl pyrrolidone (PVP) in combination with solution of silver ions and benzoic acid for the finishing of cotton fabrics to add antimicrobial characteristics to them were carried out within the framework of the research work.

A preliminary study of the literature on the use of polyvinyl pyrrolidone and silver ions in various industries as different agents allowed us to suggest the possibility of using them as components of a finishing agent [9 - 13].

Basing on preliminary experiment results the concentration of PVP varied from 4 to 8 g/l, silver ion solution (SI) from 50

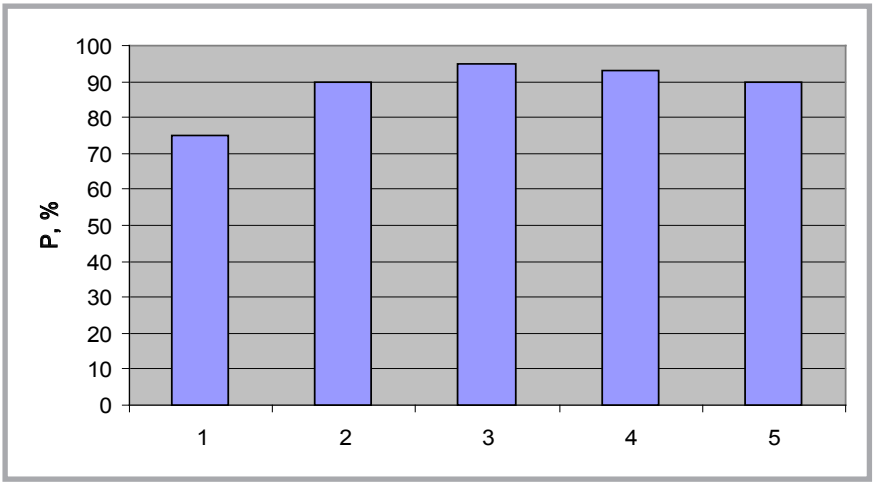

Figure 1. *Graphic of the index of resistance to microbiological distraction of cotton fabrics treated with an antimicrobial finish; 1) untreated fabric, 2) fabric finished with "Sanitised"(concentration of "Sanitised" – 2 g/l), 3) fabric finished with composition of PVP with benzoic acid and copper sulphate (concentration of PVP – 8 g/l, BA - 2 g/l, copper sulphate – 2.5 g/l), 4) fabric finished with composition of PVP with benzoic acid and silver ion solution (concentration of PVP – 8 g/l, BA – 5 g/l, SI – 100 ml/l), 5) fabric finished with composition of PVP, BA and silver ion solution after 5 washings (concentration of PVP- 8 g/l, BA - 5 g/l, SI - 100 ml/l).*

Table 2. *Indicators of strength and bioresistance of cotton fabric*

Composition No.	Concentration of components			Breaking load (prior to biodeterioration/after biodeterioration, N	Resistance to microbiological deterioration, P, %
	PVP, g/l	Silver ions, ml/l	Benzoic acid, g/l		
1	8	100	5	374/323	**92.8**
2	4	100	5	370/315	**90.6**
3	8	50	1	370/302	**86.8**
4	4	50	5	342/281	**81**
5	8	100	1	389/311	**89.6**
6	4	100	1	352/295	**84.8**
7	8	50	5	331/294	**84.6**
8	4	50	1	332/278	**80**
Unfinished fabric	-	-	-	**348/261**	**75**

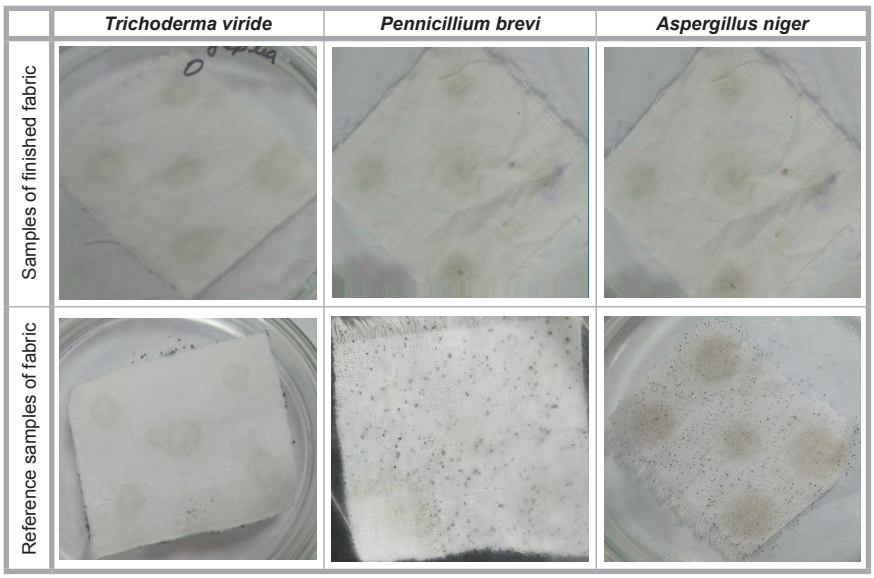

Figure 2. *Pictures of fungoid growth on the surface of cotton fabrics.*

to 100 ml/l, and the concentration of benzoic acid (BA) ranged from 1 to 5 g/l.

Strength values were evaluated on the basis of the breaking load, determined by means of the strip-breaking machine RT-250, and are presented in ***Table 2***.

Figure 1 and ***Table 2*** demonstrate that the resistance of the finished fabric to microbiological degradation compared to the untreated fabric is 1.3 times higher, which is proved by the 92.8% increase in this figure. In this case, treatment with the composition for antimicrobial finish presented was carried out at the following concentrations: 8 g/l for polyvinyl pyrrolidone, 100 ml/l for silver ions, and 5 g/l for benzoic acid.

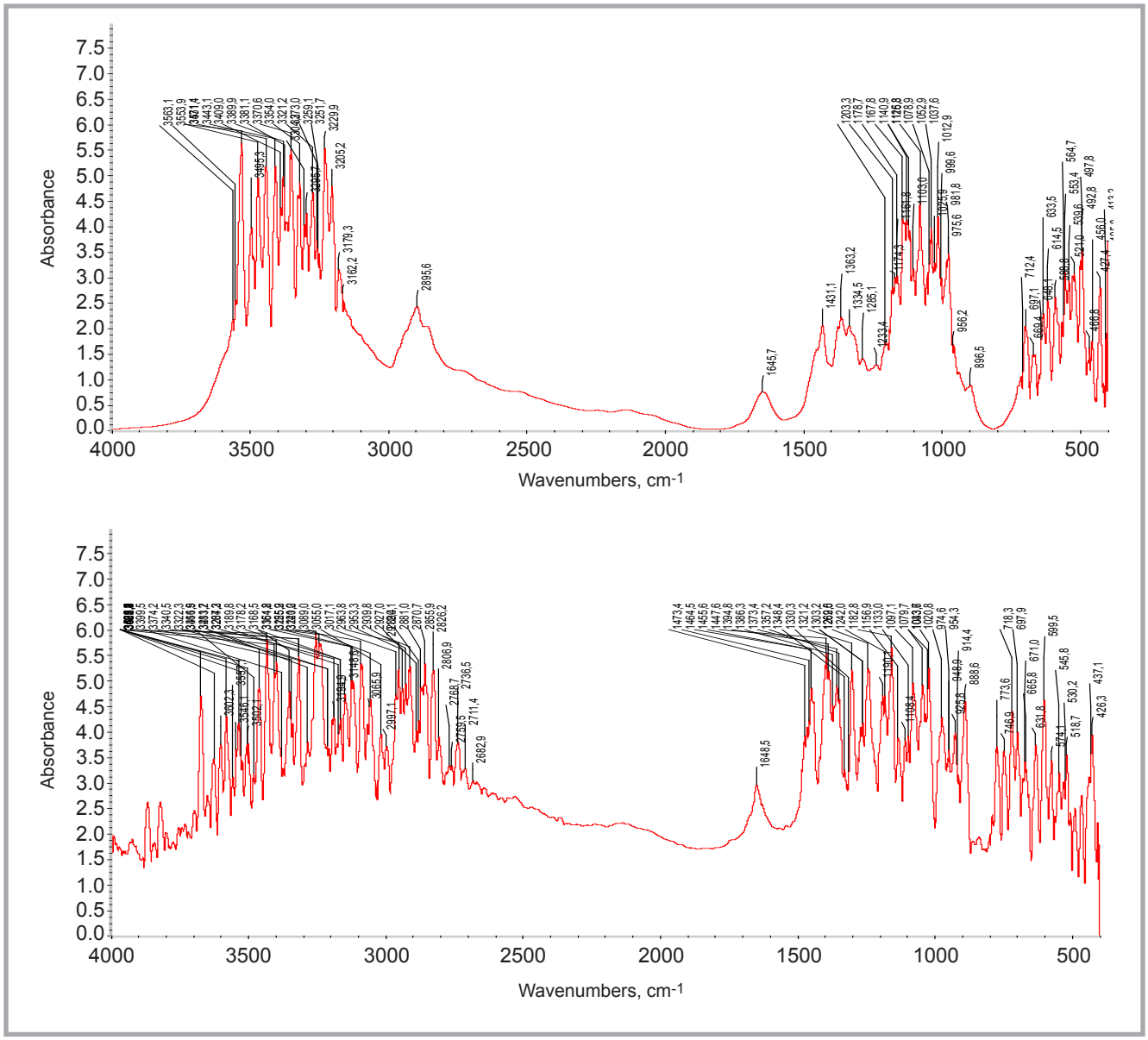

Figure 3. *IR spectra of samples of cotton fabric both untreated (a) and treated (b) with composition proposed.*

Antimicrobial properties of cotton fabric treated with the composition presented after 5 washings decrease by only 3%. The biological stability factor of the fabric finished with the composition based on PVP with benzoic acid and copper sulfate, as well as with the preparation "Sanitised", used for the antimicrobial finishing of cellulose textiles, is 95% and 90%, respectively.

In addition, microbiological studies were conducted according to GOST 9.048-89. Fabric fungus resistance tests were carried out in the following procedure. The surface of the finished and reference fabric samples was covered with water spore suspension of three fungi cultures (*Aspergillus niger, Pennicillium brevi and Trichoderma viride*) according to GOST 9.802 - 84. The results showed that *Aspergillus niger* fungoid growth was observed in the untreated control sample of fabric after 5 days. The intensity of the germination of the fungus was scored 5 points (the naked eye can clearly see the development of fungi, covering more than 25% of the test surface). In the rest of samples tested no fungoid growth was observed. The outbreak of all fungi was observed in all control samples after 28 days (***Figure 2***). The growth of fungi *Aspergillus niger* and *Pennicillium brevi* in the control samples was scored 5 points, and *Trichoderma viride* - 4 points (the naked eye can clearly see the development of fungi, covering at least 25% of the surface tested), and no outbreak of the fungi tested was observed on the surface of the finished fabric.

As is known, textile finishing with a polymer composition may lead to changes in permeability properties of the fabric. In this regard, air permeability factors were determined for different fabric samples. The air permeability factor of the cotton fabrics finished with the composition based on polyvinyl pyrrolidone, silver ion solution and benzoic acid ranges from 155 to 159 $dm^3/m^2 \times sec$, and for the reference fabric it is 162 $dm^3/m^2 \times sec$. The air permeability factors of the cotton fabric, treated with the above composition are consistent with regulatory requirements for this group of fabrics.

The data published indicate the tendency of polyvinyl pyrrolidone to form complexes with metal salts and other compounds. In this regard, IR spectra of the samples of reference and finished fabrics were examined to clarify the interaction of components in the composition (***Figure 3***). In the spectrum of the sample finished with PVP in combination with benzoic acid and solution of silver ions there were new absorption bands in the frequency range 1242 to 1269 cm^{-1}, characteristic of CN group valence vibration, as well as in the frequency ranges 1425 to 1650 cm^{-1} and 1593 to 1662 cm^{-1}, corresponding to variations of aromatic rings; bonds 2927 - 2963 cm^{-1}, corresponding to variations of CH_2 groups and 3017 - 3083 cm^{-1}, corresponding to variations of CH groups. In the frequency range of 2800 - 3500 cm^{-1} there are new absorption band, showing an increase in the number of valence vibrations of CH- and OH- groups. The band in the area of frequency of 3250 - 3300 cm^{-1} is indicative of the formation of a complex of silver with PVP - the carbonyl group of benzoic acid. IR spectra data confirm the formation of a complex between the components of the finishing composition.

The fabric samples were also examined with the help of a scanning electron microscope. As seen in ***Figure 4***, the destruction of the fabric treated with the composition caused by biological degradation is less than that of the untreated sample.

The effects of the technological parameters of new compositions for cotton fabric finishing on its biological resistance were studied using mathematical modeling.

To simulate the regression of the cotton fabric antimicrobial finishing process, the rotatable second-order plan (Box Plan), where the number of factors is K = 3 and that of experiments is 20, was used.

To simulate the regression process antimicrobial finishing of cotton fabrics, the rotatable second-order plan was used (Plan Box).

The input factors in the study of the antimicrobial finishing of cotton fabrics were as follows: x_1 – is the concentration of polyvinyl pyrrolidone in g/l; x_2 – the concentration of silver ion solution in ml/l; x_3 – the concentration of benzoic acid in g/l. Output indicator U is the coefficient of resistance to microbial degradation, P in %. Intervals and varying levels of input factors are shown in ***Table 3***.

As a result of the computer software application, regression models for substantiation of the fabric treatment parameters for the antimicrobial finish were obtained:

$$y = 93.35 + 1.717\,x_1 + 3.519\,x_2 + 2.515\,x_3 + 0.725\,x_1 x_2 - 0.175\,x_1 x_3 - 0.425\,x_2 x_3 - 1.167\,x_1^2 - 3.672\,x_2^2 - 2.649\,x_3^2$$

The regression equation for natural values of the factors after independent variable decoding is as follows:

$$P = 28.17 + 3.41\cdot PVP + 0.961\cdot SI + 3.132\cdot BA + 0.014\cdot PVP\cdot SI - 0.044\cdot PVP\cdot BA - 0.009\cdot SI\cdot BA - 0.292\cdot PVP^2 - 0.006\cdot SI^2 - 0.662\cdot BA^2$$

The multiple regression equations above demonstrate that the optimisation cri-

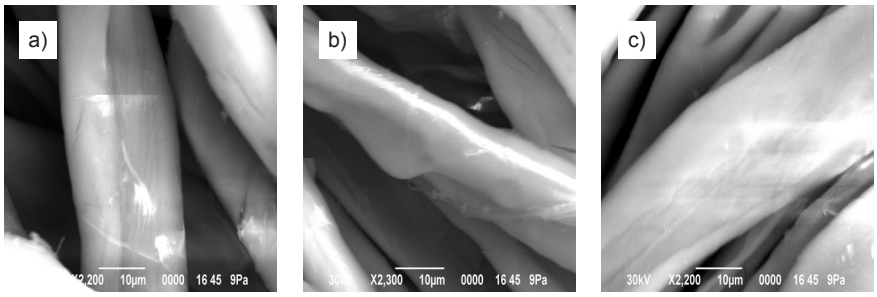

Figure 4. *Electron micrographs of cotton fabrics after biodegradation: a, b, untreated fabric, c - fabric treated with PVP, benzoic acid and a solution of silver ions.*

Table 3. *Intervals and varying levels of input factors*

Factors		Varying levels					Interval of varying
natural	coded	-1,682	-1	0	+1	+1,682	θ
Concentration of PVP, g/l	x_1	2,64	4	6	8	9,36	2
Concentration of SI,g/l	x_2	33	50	75	100	117	25
Concentration of BA, g/l	x_3	-	0	3	5	6,36	2

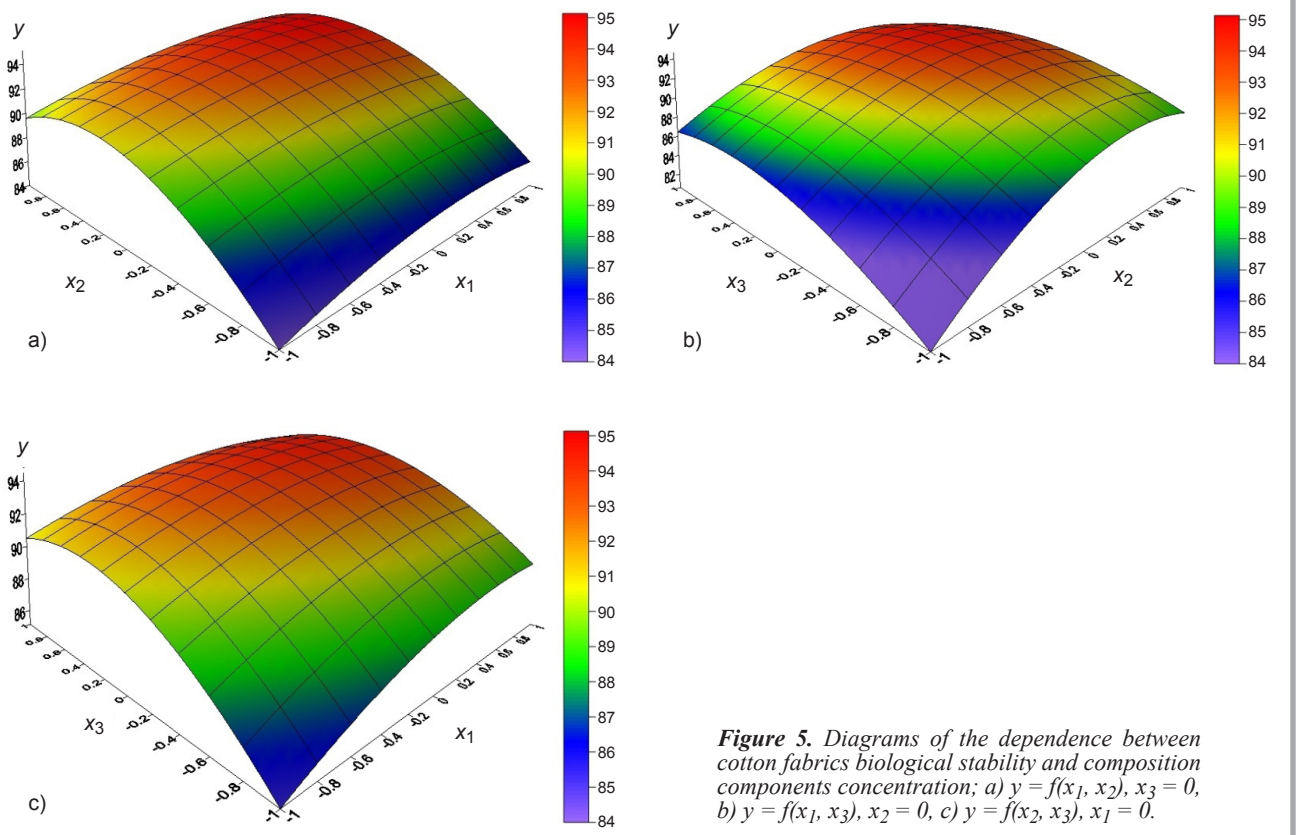

Figure 5. *Diagrams of the dependence between cotton fabrics biological stability and composition components concentration; a) $y = f(x_1, x_2)$, $x_3 = 0$, b) $y = f(x_1, x_3)$, $x_2 = 0$, c) $y = f(x_2, x_3)$, $x_1 = 0$.*

terion *U* has a significant effect on the concentration of components in the composition.

The three-dimensional graphics shown in ***Figure 5*** have been constructed to provide a clearer understanding of interrelations between the cotton fabric biological resistance indexes and composition formulation.

There is an optimum range of the concentration of PVP and benzoic acid when it is possible to maximise the biological resistance of cellulose textiles. The following optimal concentrations of the composition components are recommended for the antimicrobial finishing of cotton fabrics (***Figure 3***): PVP) 7.4 – 7.8 g/l, silver ions) 93 ml/l, benzoic acid) 4 g/l.

Conclusions

A composition consisting of polyvinyl pyrrolidone, silver ion solution and benzoic acid for the antimicrobial finishing of cotton fabrics was developed. The physico-mechanical and antimicrobial characteristics of the finished fabrics were examined using different methods of laboratory tests.

It was found that the biodegradation resistance of the finished fabric is 1.3 times higher than that of untreated ones, which is proven by the 92.8% increase in this indicator.

In addition, microbiological studies revealed that the finished fabric demonstrates no fungoid growth (*Aspergillus niger, Pennicillium brevi* and *Trichoderma viride*).

IR spectroscopic studies revealed that the antimicrobial finish makes possible the formation of a complex between cellulose, metal ions (Ag^+) and PVP, which provides an increase in the strength of the bond between the composite and fibre.

The morphological structure of cotton fibres finished with the composition discussed was studied. It was demonstrated that in the case of the antimicrobial finish, the surface of fibre not treated with the bactericidal composition is covered by mould fungi, which is not found in the treated fibre.

The technological parameters for cotton fabric finishing were developed using the application of a software package. The following optimal concentrations of the composition components are recommended for the antimicrobial finishing of cotton fabrics: PVP) 7.4 – 7.8 g/l, silver ions) 93 ml/l, and benzoic acid) 4 g/l.

Thus it was found that cotton fabrics finished with the composition based on polyvinyl pyrrolidone, silver ion solution and benzoic acid have advanced antimicrobial characteristics preventing fouling with mould fungi and are not deteriorated by microorganisms under operation conditions.

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