STUDY OF THE INFLUENCE OF ANTIMICROBIAL AGENTS ON THE OPERATIONAL AND HYGIENIC PROPERTIES OF CELLULOSE MATERIALS

Olga Paraska[1], Hrystyna Kovtun[2], Lubos Hes[3], Serhiy Horiashchenko[1]
[1] Khmelnytskyi National University, Instytutska Street 11, Khmelnytskyi, UKRAINE
[2] Khmelnytskyi Lyceum of II-III degrees of Khmelnytskyi Regional Council, Ozerna Street 14, Khmelnytskyi, UKRAINE
[3] Technical University of Liberec, Faculty of Textile Engineering, Studentska 1402/2, Liberec, CZECH REPUBLIC
olgaparaska@gmail.com, hrystynak2006@gmail.com, lubos.hes@gmail.com, gsl7@ukr.net

Abstract: *At the present stage of development of society, in pandemic conditions, people are experiencing the growing influence of man-made factors (energy flows of internal and external origin, ionizing radiation, etc.), some drugs, pathogenic microflora (fungi, viruses, bacteria, intracellular parasites). The origination of a critical mass of parasitogens can be prevented by using, in addition to traditional methods of prevention and treatment, textile materials with certain additional properties obtained by antimicrobial treatment. The aim is to study the change in the operational and hygienic properties of cellulosic materials after treatment with antimicrobials. To assess the effect of antimicrobials (biguanide derivatives and quaternary ammonium salts) on the operational and hygienic properties of cellulosic materials (cotton fabric) the following indicators were taken into account: strength, stiffness, wrinkle recovery, capillarity of materials, structural and morphological characteristics. The results of research have confirmed the possibility of using solutions of antimicrobial agents for effective processing of wares, without destructive effects on the structure of cellulosic materials; allowed to introduce a research methodology to provide antimicrobial properties of cellulosic materials of different assortment.*

Keywords: *antimicrobial agents, cellulose, cotton, antimicrobial textiles, biguanide derivatives, quaternary ammonium salts.*

1 INTRODUCTION

Providing consumers with safe goods is one of the urgent scientific and practical problems, as its solution depends on human health, welfare and quality of life. In the ranking of consumer activity, the textile market occupies one of the main places. This is primarily due to the fact that the population is growing and increasing demand for textile products, including cellulosic wares (Figure 1) [1, 2].

One of the most common types of destruction of textiles during operation and under the influence of external factors is microbiological destruction, which occurs due to the amplification of three main types of microorganisms: bacteria, actinomycetales and fungi. On the surface of any textile fiber can be found microflora, which at high relative humidity and optimum temperature for its development is able to eventually absorb the fibers as a nutrient substrate and cause their destruction.

Textiles based on natural fibers, such as cellulosic materials, are most susceptible to microbiological damage. Excessive growth and development of microorganisms on materials leads to deterioration of their operational properties and reduction the term of use of textile products. Therefore, the current problem of the textile industry is the choice and use of biocidal products that would not only destroy unwished microorganisms, but also do not impair the quality characteristics of materials and products.

Currently, the textile industry is actively searching for the most advanced and environmentally friendly substances for the manufacturing of resistant cellulosic materials for various functional purposes.

Many scientific works [3-5] have been devoted to the development of materials with antimicrobial properties, in which it is proved that the creation of such products is possible with the use of antimicrobial biocidal agents that do not reduce their operational and hygienic properties.

There are basic requirements to be satisfied by an antimicrobial agent for its successful application on cellulose materials. The basic requirements of an antimicrobial agent for cellulose materials are summarized below [3, 6, 7]:

- suitable for cellulose materials processing;
- be easy to apply on textile substrates;
- be able to inactivate undesirable microbes while simultaneously not affect desired microbes;
- safe for use on skin or area of application;

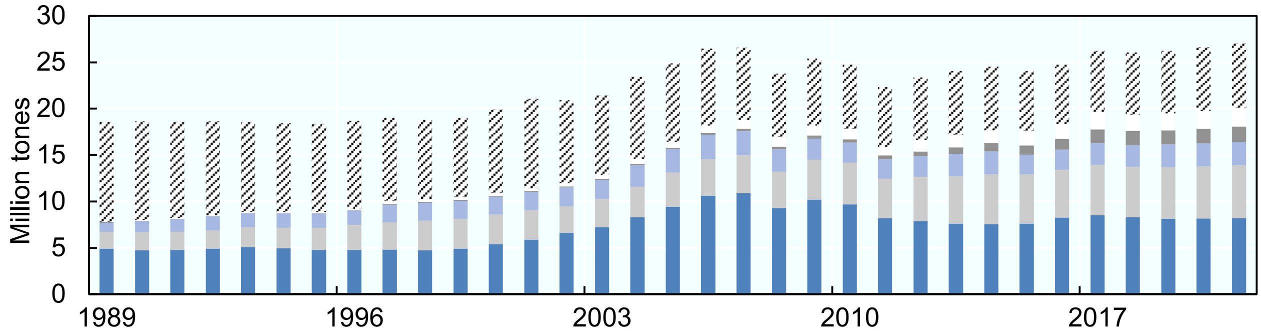


Figure 1 Usage dynamics of cellulosic materials in the world (million tons) in the period from 1989 to 2021: -China; -India; - Pakistan; - Viet Nam; - Bangladesh; - Rest of the World.

- inert to chemicals to which the cellulose materials might be exposed during processing;
- durable to repeated laundering, dry cleaning, ironing and prolonged storage including resistance to detergents used to care for the textiles;
- stable during usage without degrading into hazardous secondary products;
- -conducive to the environment.

These requirements are always counterbalanced by a need for frugality and budgetary constraints.

Most antibacterial agents applied on cellulose materials have been used for many years in food preservatives, disinfectants, and wound dressings. The attachment of these compounds to textile surfaces or their binding with the fiber can reduce their activity largely and limits the antibacterial agents' availability. In addition, the antibacterial agent can gradually be lost during the washing and use of the textile material. The most widely used antimicrobial agents for cellulose materials are based on metal salts, quaternary ammonium compounds, halogenated phenols, polybiguanide, chitosan, and N-halamines [3, 7, 8].

In general, antibacterial agents can either kill the microorganisms (−cidal) or inhibit their growth (−static). Almost all the commercial antimicrobial agents used in cellulose materials, (polyhexamethylene biguanide, quaternary ammonium compounds, and triclosan) are biocides. They can damage the cell wall or disrupt the cell membrane permeability, and inhibit the activity of enzymes or synthesis of lipids [6].

The antibacterial material can be separated in two categories: antimicrobials with controlled release or leaching mechanism and bound or non-leaching type antimicrobials. The mechanism of the leaching type will act upon contact of the cell. On the other hand, the non-leaching types will diffuse a disruptive chemical to the cell. This type is preferred for an environment supporting the diffusion of the chemical, such as water. The non-leaching type antimicrobials (quaternary ammonium compounds, polyhexamethylene biguanide) are chemically bound to the textile substrate. Hence, the antimicrobial can act only on the microbe that are in contact with the treated textile's surface. By virtue of its binding nature, these antimicrobials are not depleted and therefore potentially may have higher durability.

For the purpose of antimicrobial treatment are used traditional biocidal substances, which are not always quite effective and can have toxic effects on consumers and the environment. Therefore, the presented research is devoted to the search for safe for humans and the environment, approachable antimicrobial agents, and the study of their impact on the operational and hygienic properties of cellulosic materials. To assess the effect of antimicrobials (biguanide derivatives and quaternary ammonium salts) on the operational and hygienic properties of cellulosic materials (cotton fabric) the following indicators were taken into account: strength, stiffness, wrinkle recovery, capillarity of materials, structural and morphological characteristics [9-11].

2 EXPERIMENTAL PART

2.1 Materials used

The studies used antimicrobial agents of Ukrainian production, which have high efficacy and a wide range of indications for use - biguanide derivatives and quaternary ammonium salts (Table 1).
Studies of the efficiency of antimicrobial agents were performed on specimens of cotton fiber fabrics, which are presented on the market of Ukraine (Table 2).

2.2 Research methods

The change in mechanical properties of cotton fabrics after treatment with solutions of antimicrobial agents (biguanide derivatives; quaternary ammonium salts) was determined according to standard methods DSTU ISO 13938-1:2007, DSTU ISO 13938-2:2007 [12 – 14].
The assessment of the change in the mechanical properties of cellulosic materials was carried out according to the indicators of bursting strength P_p [N] and bursting distension l_p [mm].

Bursting strength directly reflects the durability index of the fabric when it is deformed and ruptured by external force.

Table 1 Physico-chemical parameters of antimicrobial agents

Parameters of agents	Biguanide derivative	Quaternary ammonium salt
IUPAC name	N,N′′′′1,6-Hexanediylbis[N′-(4-chlorophenyl)(imidodicarbonimidic diamide)]	10-[dimethyl-[2-(5-methyl-2-propan-2-ylcyclohexyl)oxy-2-oxoethyl] azaniumyl]decyl-dimethyl-[2-(5-methyl-2-propan-2-ylcyclohexyl)oxy-2-oxoethyl]azanium; dichloride
Chemical formula	$C_{22}H_{30}Cl_2N_{10}$	$C_{38}H_{74}Cl_2N_2O_4$
Physical properties	Clear colorless, odorless liquids	
Antimicrobial effect	Has a rapid and distinct effect on gram-positive and gram-negative bacteria, yeast and dermatophytes.	Has a distinct bactericidal effect on Staphylococcus, Streptococcus, Corynebacterium diphtheriae, Pseudomonas aeruginosa, capsular bacteria; fungicidal effect on yeast, yeast-like fungi, pathogens of mycosises; antiseptic effect on Trichomonas, Giardia; virucidal effect on viruses.
Manufacturer	LLC "DKP "Pharmaceutical Factory", PJSC Pharmaceutical Factory "Viola", LLC "MEDLEV", LLC "Pharma Cherkass", LLC "Kilaff"	LLC "Yuriya-Pharm"
Cost, l/USD	3-5,5	12,5-14
Expiration date	3 years	3 years

Table 2 Parametrs of the studied cellulosic materials

The name of the fabric	Composition	Width, [cm]	Weave	Areal density, [g/m^2]	Density		Porosity, [%]	Yarn linear density [tex]	
					Weft [wefts/cm]	Warp [warps/cm]		Weft	Warp
Cotton fabric	Cotton 100 %	150	Plain-weave	180	22	41	68	37	37

Pneumatic method was used for the determination of bursting strength and bursting distension of the samples. The fabric bursting strength and bursting distension was tested using a PT-250 tester machine according to the DSTU ISO 13938-2:2007 (sample size 200x50 mm) testing method. Strain measurement range from 0 to 200 mm. The scale division of the strain gauge is 1 mm. Limits of the permissible value of the error of the measuring device of the movement of the active grip ± 1 mm. The range of task speeds of movement of the active gripper during the working stroke is from 25 to 250 mm/min. The distance between the grips (initial) is adjustable, in 50 mm intervals in the range from 0 to 450 mm, with an error of ±1 mm. The working stroke of the active grip is at least 200 mm. Ten samples were tested from each group and expressed in N. All the tests were performed under standard atmospheric conditions (temperature: 20 ± 2 ºC and relative humidity: 65 ± 2%).

The stiffness of cellulosic materials is determined by the console method (under the effect of the own weight of the distributed load) [15]. A sample of appropriate size is placed on the gear of the device so that on its side faces were placed the ends of the sample length of 7 cm. When lowering the side faces of the device, the ends of the sample, which lost resistance, bend. Using the scale of the device, which is located along the side faces, the absolute deflection of the ends of the sample is measured, the relative deflection is calculated by its value according to the formula:

$$f_0 = f/l, \quad (1)$$

where: f_0 - relative deflection of the ends of the sample; f - the absolute deflection of the ends of the sample, [cm]; l – the length of the ends, [cm].

$$l = (Z_0 - a)/2, \quad (2)$$

where: Z_0 - length of the sample, [cm]; a – the length of the fixed part of the surface, a = 2 cm.

The coefficient A of relative deflection of the ends of the sample is determined in the reference book by the value of the relative deflection f_0. The fabric stiffness coefficient EI [μN/cm^2] is calculated by the formula:

$$EI = 42046\, m/A, \quad (3)$$

where: m – the mass of five samples.

Wrinkling of sample of cellulosic materials is determined by the method of oriented wrinkling according to DSTU 4143-2002/GOST 31101-2003 [9, 16]. The essentiality of this method is that the sample of T-shaped material is bent at an angle of 180°and loaded for 15 minutes. In 5 min after removal of load, the coefficient of wrinkle recovery K_N according to the formula is defined:

$$K_N = \alpha \frac{100}{180}, \quad (4)$$

where: α – the recovery angle of the sample.

To assess the hygienic properties of the studied specimens after treatment with solutions of antimicrobial agents, the capillarity of materials was determined. The capillarity of textile products characterizes the absorption of moisture by the lengthwise capillaries of the material and is estimated by the height h, [mm] of lifting the liquid in the sample, immersed at one end in the liquid for 1 hour. Capillarity is determined in accordance with the requirements of DSTU GOST 3816:2009 [10, 17, 18].

All measurements were repeated 10 times (n = 10) and that mean values together with 95% confidence intervals are shown to enable comparison of sample properties after exposure to the chosen antimicrobial agents.

3 RESULTS AND DISCUSSION

According to the results of the study of the mechanical properties of cotton samples after treatment with solutions of antimicrobial agents (Table 3), it can be observed that after the treatment of biguanide derivatives, the bursting strength was even slightly increased in warp direction and decreased in weft direction. The strength in warp direction was not affected, while it slightly decreased when applying treatment by quaternary salts compared to strength of untreated fabric. The decrease was less than 10 % in both cases compared to the untreated fabric.

After 10 days of exposure in the substrate (substrate simulates soil microflora, contains sand, horse manure and garden soil; substrate humidity 30 ± 5%, pH 6-7.5) the strength of the untreated samples was reduced by half (from 464 N and 430 N to 235 and 205 N) It was expected that usage of antimicrobial agents could reduce this significant degradation of the fabric in the substrate. From tests performed, it is visible that the application of both antimicrobial treatments increases the strength compared to the untreated fabric after placement the fabric in the substrate.

When comparing strength of original fabric and strength of treated fabric after the exposure in the substrate, the decrease of the strength is around 30%. In the case of the biguanide derivatives, the strength in warp direction is reduced only by 23 %. From the perspective of this test, it appears that a higher average bursting strength is achieved by using biguanide derivatives compared to quaternary ammonium salts as antimicrobial agents.

The bursting distension of the weft samples is greater than the warp, due to the fact that the weft threads are more curved than the warp threads. According to Table 4, it can be observed that after the treatment of biguanide derivatives, the bursting distension was increased in warp direction from 10 mm to 14 mm and was not changed in weft direction - 25 mm. The bursting distension was even slightly increased in warp direction from 10 mm to 12 mm, while it slightly decreased - form 25 mm to 24 mm in weft direction when applying treatment by quaternary ammonium salts compared to bursting distension of untreated fabric.

Table 3 Bursting strength (P_p, [N]) of cotton samples (mean values)

The sample of material	Bursting strength, P_p, [N]		Bursting strength, P_p, [N], after 10 days of exposure in the substrate	
	warp	weft	warp	weft
Untreated fabric	464±11.20	430±10.75	235±5.88	205±5.13
Treated with biguanide derivatives	496±12.40	392±9.80	316±7.90	329±8.22
Treated with quaternary ammonium salts	458±11.45	402±10.05	319±7.98	296±7.40

Table 4 Bursting distension (l_p, [mm]) of cotton samples (mean values)

The sample of material	Bursting distension, l_p, [mm]		Bursting distension, l_p, [mm], after 10 days of exposure in the substrate	
	warp	weft	warp	weft
Untreated fabric	10±0.25	25±0.63	17,5±0,44	25±0.63
Treated with biguanide derivatives	14±0.35	25±0.63	16±0.40	19±0.48
Treated with quaternary ammonium salts	12±0.3	24±0.6	15±0.28	26±0.65

Table 5 Stiffness (EI, [μN·cm^2]) and wrinkle recovery (α, K_N, [%]) of cotton samples (mean values)

The sample of material	EI, [μN·cm^2]		α, [%]		K_N, [%]	
	warp	weft	warp	weft	warp	weft
Untreated fabric	5773±144.3	1945±48.6	64±1.6	56±1.4	35,56±0.89	31,11±0.78
Treated with biguanide derivatives	4253±106.3	1752±43.8	66±1.65	54±1.35	36,67±0.91	30,00±0.75
Treated with quaternary ammonium salts	6621±165.5	2124±53.1	62±1.55	59±1.48	34,44±0.86	32,78±0.82

After 10 days of exposure in the substrate (substrate simulates soil microflora, contains sand, horse manure and garden soil; substrate humidity 30 ± 5%, pH 6-7.5) the bursting distension was increased in warp direction for all samples. The bursting distension was decreased in weft direction from 25 mm to 19 mm, when applying treatment by biguanide derivatives. After the treatment of quaternary ammonium salts the bursting distension was slightly increased in weft direction from 24 mm to 26 mm. From tests performed, it shows that a higher average bursting distension is achieved by using quaternary ammonium salts compared to biguanide derivatives as antimicrobial agents after placement the fabric in the substrate.

Analysis of the stiffness (according to equation 3) of cotton samples after treatment with antimicrobial agents (Table 5) shows that treatment with solutions of biguanide derivatives reduces the stiffness of materials from 5773 μN·cm^2 to 4253 μN·cm^2 in the warp direction and from 1945 μN·cm^2 to 1752 μN·cm^2 in the weft direction. When treated with solutions of quaternary ammonium salts, the stiffness of the test samples increases from 5773 μN·cm^2 to 6621 μN·cm^2 in the warp direction, and from 1945 μN·cm^2 to 2124 μN·cm^2 in the weft direction.

The study of the wrinkle recovery of cotton samples showed (Table 5) that the recovery of the warp samples in comparison with the recovery on the weft is faster, due to the elastic deformations of the warp threads. Compared with the untreated samples, changes in the wrinkling of the samples after treatment with antimicrobial agents are insignificant and the coefficient of wrinkle recovery (K_N, [%]) (4) is 30 % - 36.7 %, in accordance.

Thus, antimicrobial treatment with products based on biguanide derivatives is recommended for underwear products, and treatment with quaternary ammonium salts – for form-resistant products (shirts, corporate clothing).

Hygienic properties of cellulosic materials after treatment with antimicrobial agents were determined by the hygroscopicity of fabrics [10]. Table 6 shows the results of capillarity studies of products (h, [mm]), which characterizes the hygroscopicity of cellulosic materials.

As can be seen from Table 6, the untreated fabric has low capillarity, due to the fact that the pores contain residues of concomitant and finishing substances that prevent the penetration of liquid into the textile material.

Table 6 The influence of antimicrobial agents on the capillarity (h, [mm]) of samples of cellulosic materials (mean values)

The sample of material	Capillarity, h, [mm]	
	warp	weft
Untreated fabric	16±0.42	14±0.35
Treated with biguanide derivatives	44±1.1	44±1.1
Treated with quaternary ammonium salts	70±1.75	55±1.38

For weft samples were observed less distinct changes in capillarity than for warp samples, which may be due to differences in warp and weft yarn structure. It is established that the use of antimicrobial agents improves the capillarity of cellulosic materials from 44 mm to 70 mm. The capillarity of cellulosic materials treated with quaternary ammonium salts is greater than that of biguanide derivatives, and is 70 mm in the warp sample and 55 mm in the weft sample.

Studies show that antimicrobial agents remove impurities and other substances remaining on the fabric during its exploitation, ie there occurs a cleaning of pores on the surface of cellulosic materials, which improves the hygienic properties of textiles.

Using a microscope Hirox® KH-8700, was observed a relief image (microscope images of samples at ×800 total magnifications) of the surface of cotton fabrics without treatment with antimicrobial agents and treated with solutions of selected antimicrobials (Figure 2). Image analysis shows that the surface of materials after treatment with antimicrobial agents is resistant to damage by microorganisms, due to the adsorption of antimicrobial substances on fabrics [11].

The decrease in the strength of textile materials that have defects in the structure, with increasing degree of crosslinking of macromolecules can be explained by the fact that due to the compaction of the inner layers of the fiber may increase the size of microcracks inside the fiber, leading to loss of the strength. Therefore, the influence of antimicrobial agents on the structure of cellulosic materials was studied using IR spectroscopy. The results of spectral analysis are shown in Figure 3.

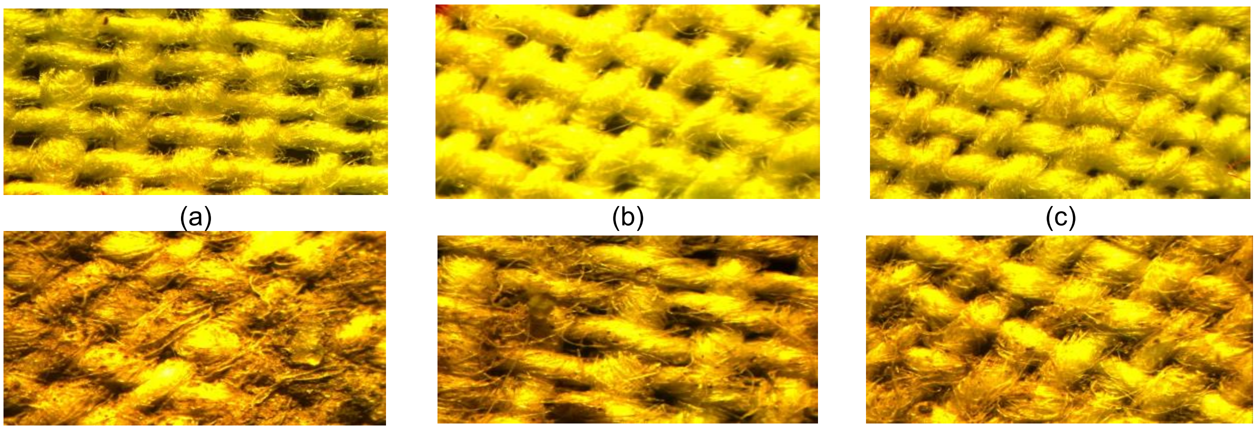
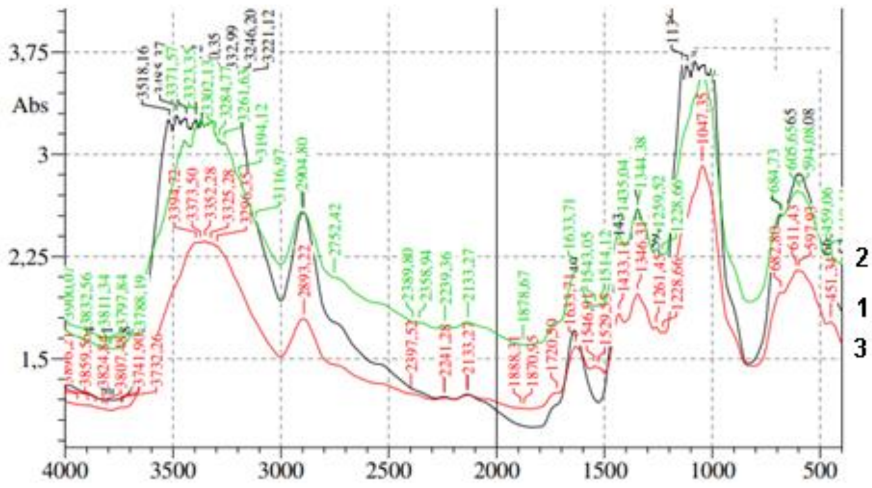


Figure 2 Image of the surface of cotton materials after treatment with antimicrobial agents (microscope images of samples at ×800 total magnifications): (a) untreated warp sample, (b) sample treated with a solution of biguanide derivative, (c) sample treated with a solution of quaternary ammonium salts, (d) untreated sample after exposure in the substrate, (e) sample treated with a solution of biguanide derivative after exposure in the substrate, (f) sample treated with a solution of quaternary ammonium salts after exposure in the substrate



Wavenumber, cm^{-1}

Figure 3 IR spectra of cotton materials after treatment with antimicrobial agents: 1 - the untreated sample, 2 - treatment with a solution of a biguanide derivative, 3 - treatment with a solution of quaternary ammonium salts

Analysis of the IR spectra of the untreated and treated samples showed that the valence vibrations of the -OH bond of different groups (primary, secondary, tertiary) have maxima of approximately equal intensity: 3329 cm^{-1} - primary -OH and 3284 cm^{-1} - secondary -OH. Valence oscillations of C-O of different groups (C-OH - primary, OH - secondary, C-O-C - cyclic, C-O-C - intercyclic (glycosidic bond), are manifested in the range from 1047 to 1228 cm^{-1} as a complex strip with several maxima corresponding to these connections.

Thus, the analysis showed that the samples contain primary and secondary OH groups, which have the ability to form a hydrogen bond of different strength. Primary groups form such a bond faster, but it is weaker in strength, and secondary groups are slower, but the bond is stronger. This is what provides the ability of antimicrobial agents to be well absorbed and retain on the surface and inside the fiber molecules due to hydrogen bonds.

4 CONCLUSION

Studies confirm the feasibility of using antimicrobial agents – biguanide derivative and quaternary ammonium salts – for antimicrobial treatment of cellulose products, without destructive effects on the structure of textiles.

Analysis of the evaluation of the operational properties of cotton materials after treatment with antimicrobial agents at all levels of the structure of fabrics, allows to propose a methodology for studying the properties of a wide range of textiles, as these factors will affect the extension of the service life of textiles, reducing the amount of textile waste.