EurAsian Journal of BioSciences
Eurasia J Biosci 14, 4029-4034 (2020)

The use of biocides for rendering polyamide materials antimicrobial

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Abstract

The paper studies the questions of the use of antimicrobial products (biocides) which can increase resistance of textile materials to the action of microorganisms and confer antimicrobial properties. Antimicrobial textile materials have broad opportunities of use both for daily and technical purposes. Hence, the development of efficient products for rendering textiles antimicrobial and enhancing their biostability against widespread microorganisms is relevant. The objective of the conducted research was chemical modification of polyamide textile materials with biocides and evaluation of antimicrobial properties of the resulting materials. Textile polycaproamide yarns and nonwoven materials were selected as the research object. During the experiment, the test portions under study were treated with biocides: nitrofuryl-acrolein, chloramine B, and catamine AB. Then, the direct action of the test portions on live cells growing on the nutrient medium was evaluated. Antimicrobial activity was identified according to the area of sterile zones which were formed around test portions. The research results have shown that the greatest antimicrobial action was observed in test portions treated with nitrofuryl-acrolein (NFA) and catamine AB. It has been shown that antibacterial action (bacterial growth inhibition zone) of yarns chemically modified with NFA amounts to: 14,3 mm when acting on the Erwinia herbicola bacteria, while it is 24,1 mm when acting on the Bacillus mesentericus bacteria. NFA-containing nonwoven polyamide materials had the diameter of sterile zones ranging from 21,4 to 24,9 mm with gram-negative bacteria, and from 32,3 to 36,4 mm – with the gram-positive ones (under the action of the 250 g/m^2 surface density material). It has also been found out that the said materials feature fungicidal action - after two days of exposure to the standard set of microscopic fungi, these fabrics had the fungicidal action zone diameter equal to 39,0 mm; in 8 days, the diameter of the zone was 2 times smaller; however, asporogenous mycelium was observed around the test portions, which gives evidence about fungistatic action of these materials. In the work, chemical modification of polycaproamide yarns and nonwoven materials with nitrofuryl-acrolein (NFA) has been performed. The research results have shown that both yarns and nonwoven materials made of polycaproamide containing NFA have antimicrobial activity both against bacterial cultures, and against microscopic fungi.

Keywords: biocides, yarns, nonwoven materials, antimicrobial properties, protection of fibrous materials, catamine B

Pekhtasheva E, Raykova E, Polozhishnikova M, Utkina A (2020) The use of biocides for rendering polyamide materials antimicrobial. Eurasia J Biosci 14: 4029-4034.

INTRODUCTION

Antimicrobial textile materials have become widely used in various areas. The most well-known agents for suppressing life activity of pathogenic microorganisms are antimicrobial substances applied on textiles. The principal problem in creating such materials is the loose fixation of antimicrobial products (biocides) on textiles. Application and further fixation of antimicrobial products on nonwoven textile materials are of special interest. This is associated with the domain lacking research, which confirms the relevance of this work.

The principal method for enhancing biostability of textiles is the use of antimicrobial products (biocides) (Buzov et al., 2004). However, it should be noted that so far, there has been no “perfect” biocide which would both ensure reliable protection of materials and meet a number of other requirements.

The requirements for a “perfect” biocide for textile materials are as follows (Pekhtasheva, 2020): efficient action against the most widespread microorganisms at minimum concentration and maximum duration of action; nontoxicity of the concentrations used for people; absence of color and smell; low cost and convenience of application; no deterioration of physical and mechanic, hygienic, any other properties of the items; compatibility

Received: November 2019
Accepted: March 2020
Printed: October 2020

with other finishing products and auxiliary substances for textiles; good light-fastness and outdoor stability.

LITERATURE REVIEW

Methods for rendering textile materials antimicrobial and biostable used in Russian and foreign industry can be grouped as follows (Pekhtasheva, 2020; Mikheeva, Ilyushina & Krasina, 2019):

- impregnation with biocides, chemical and physical modification of fibers and yarns to be formed up into textile materials;
- impregnation of textile fabric with antimicrobial product solutions or emulsions, its chemical modification;
- introduction of antimicrobial products into binders (in manufacturing nonwoven materials by the chemical method);
- conferring antimicrobial properties to textiles during their dyeing and finishing treatment (Razuvaev, 2010);
- using disinfectant substances in chemical cleaning or washing of textile items.

Impregnation of fibers and the very textile fabrics, however, does not ensure the reliable fixation of treating agents, due to which antimicrobial action of such materials is not lasting. The most efficient methods for rendering textiles biocidal are ones that ensure the formation of a chemical bond between the biocide and the material of the item, i.e., chemical modification methods. The methods of chemical modification of fibrous materials include the ways of treatment that result in creating inclusion compounds, such as, for example, introducing biologically active products into spinning melts or solutions, and chemical fixation of products.

Almost each class of chemical compounds has been used for conferring antibacterial or antimycotic activity to textile items at a certain point of time. Currently, there is a broad range of natural and synthetic products inhibiting the development of pathogenic microflora. Some of them cause its total elimination. The disadvantage of these products is their toxicity for humans. This is why the determining condition in selecting substances and technologies for modification of consumer industry materials or items is their environmental safety (Krichevsky, 2011; Safonov & Dmitrieva, 2012; Dmitrieva, 2017; Perelshtein, 2008; Volf, 1980; Illarionova & Grigoriev, 2016; Hamlyn, 1983; Hofman, 1986).

Historically, salts of copper, silver, tin, mercury, etc. were used for protection of fibrous materials against biodeterioration. It was salts of copper that became the most widely used ones of these biocides owing to their low cost and a relatively low toxicity. The use of zinc salts is limited by their low biocidal action, while that of mercury, tin, and arsenic salts – by their high toxicity for humans (Volf, 1980; Illarionova & Grigoriev, 2016). However, there is information that for synthetic and natural fibrous materials used in linings and removable shoe insoles, organomercurial products have been developed and extensively advertised for antibacterial and antimycotic treatment (Vigo & Benjaminson, 1981).

There are data in literature (Elaine & Mc. Carthy, 1998; Volf & Meos, 1971) on rendering textiles bacteriostatic by impregnating them with a mixture of neomycin salts with tartaric, propionic, stearic, phtalic and some other acids. They were dissolved in water, methanol or butanol and applied on the materials by spraying the solutions.

A method of bactericidal treatment of textile materials with solution of hexachlorophene in organic solvents or water emulsions dispersed using nonionic detergent was suggested (Hofman, 1986).

When manufacturing capron, at the polymerization stage, an antibacterial agent is added which represents an organotin compound (probably, tributyltin oxide or hydroxide), which ensures retaining the antibacterial effect after repeated washing (Volf, 1980; Illarionova & Grigoriev, 2016).

There were developed methods for rendering textile materials antimicrobial by introducing nitrofuran products into spinning melts and subsequently fixing them in the fine structure of fibers during forming, similarly to inclusion compounds (Volf, 1980; Illarionova & Grigoriev, 2016; Volf & Meos, 1971).

Physical modification of fibers or yarns is the focused modification of their composition (without new chemical formations and transformations), structure, and properties by modifying the production technology. Improving the structure and enhancing the extent of crystallinity of fibers lead to higher biostability (Komarovskaya et al., 2020).

However, unlike the chemical one, physical modification does not confer any antimicrobial properties to fibers.

As previously noted, there are various methods to protect materials against attack by microorganisms. Meanwhile, the most efficient one is treatment with biocides (Pekhtasheva et al., 2012).

With regard to this, the authors faced the task of selecting biocidal agents and methods for manufacturing antimicrobial textiles. Selection of possible areas of the practical use of materials having antimicrobial properties is important, too.

Fibrous textiles containing nitrofuryl-acrolein (NFA) are known to have the pronounced antimicrobial effect while producing no significant negative impact on the human organism (Volf, 1980; Illarionova & Grigoriev, 2016; Volf & Meos, 1971). This is why the study of the opportunities of using this biocide for modification of polycaproamide yarns is of interest.

Table 1. Indicators of physical and mechanic properties of nonwoven needled polyamide materials*

Test portion	Surface density, g/m^2	Force at rupture, N		Elongation at rupture, %	
		length	width	length	width
No. 1	535	1050	486	94,8	118,6
No. 2	250	347	461	70,9	117,7

* Developed by the authors

Table 2. Conditions of treatment of PCA yarns and nonwoven materials with biocides*

Conditions of treatment	Nitrofuryl-acrolein (NFA)	Chloramine B	Catamine AB
Bath concentration	0,2%	1,0%	3,0%
	0,6%		
	1,0%		
Treatment temperature	50–55ºC	70ºC	30°C
Duration of modification	260–280 min	60 min	30 min
Catalyst	CH_3COOH – 3%	–	–
Bath ratio	40	5	20

* Developed by the authors

MATERIALS AND METHODS

The objective of the research conducted was to evaluate antimicrobial properties of polyamide textile materials chemically modified with biocides. Caproamide yarns and needled nonwoven materials were selected as test portions.

For achieving the set objective, a number of tasks have to be completed:

analyzing antimicrobial compounds applied on caproamide textile materials;

conducting treatment and modification of capron yarns and nonwoven materials;

studying antimicrobial properties of polycaproamide (PCA) yarns and nonwoven materials;

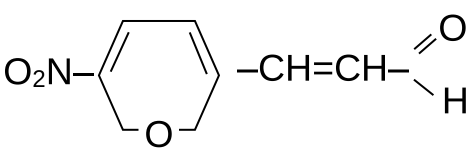
exploring the action of textile materials modified with biocides on bacteria and microscopic fungi.

The research was conducted using capron (polycaproamide) yarns of the 15,6 tex linear density (GOST 15897-97, 2019). Fibrous nonwoven materials of polycaproamide fibers obtained from the secondary PCA melt of the 0,7 and 0,3 tex linear density were included into the research. The web was linked mechanically with needle punchers. **Table 1** gives the principal parameters of nonwoven PCA fabrics included into the research.

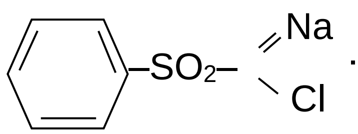
Analysis of antimicrobial substances included into the research

The capron yarns under study were subjected to treatment with the following biocides: β-(5-nitrofuryl-2)-acrolein, chloramine B, catamine AB.

1. A high antimicrobial activity is featured by β-(5-nitrofuryl-2)-acrolein (NFA). It is the intermediary product in the synthesis of furazolidone. Its formula is as follows:



2. Benzenesulfo-sodium chloramide (chloramine B) has an antiseptic, deodorizing action, and the following formula:



The possibility of treating polyamide fibers with chloramine B (benzenesulfo-sodium chloramide) containing available chlorine was studied. This product was selected because it is an easily accessible commercial substance having a pronounced disinfecting effect and low cost.

3. Catamine AB biocide was also included into the research. It belongs to the class of quaternary ammonium compounds and to cationic surfactants (Volf, 1980). It is characterized by a high antimicrobial effect and simplicity of use (it is highly soluble in water).

Catamine AB (alkyldimethylbenzylammonium chloride) – antimicrobial agent of a broad coverage – has the following structural formula:

$[C_nH_{2n+1}N(CH_3)_2CH_2C_6H_5]^+CL^-$,

where $n = 10^{-18}$.

Catamine AB (TU 9392-003-48482528-99) is the Russian analog of Roccal produced by the English company Unitron; the commercial product is the 49% water solution of alkyldimethylbenzylammonium chloride. This product belongs to cationic surfactants and has bactericidal action.

The treatment and modification of capron yarns were conducted under the following conditions (**Table 2**).

After the treatment in the modifying NFA bath, the fibrous materials were carefully flushed with hot water to remove any NFA not having reacted and air dried.

The treated test portions were air dried at t =25°C.

Fibers kept in water at the same temperature modes were used as the control.

The study of antimicrobial properties of PCA yarns and nonwoven materials

As the agents of microbiological action, the strains of bacteria received from the archive of the All-Russian Research Institute for Agricultural Microbiology (Pushkin, Leningrad Region) were used: *Bacillus subtilis*

Table 3. Antibacterial properties of yarns treated with biocides*

Products	Concentration of biocide, %	Diameter of the bacterial growth inhibition zone, d, mm				
		Bacillus subtilis	Pseudomonas fluorescens	Erwinia herbicola	Bacillus megatherium	Bacillus mesentericus
NFA	0,2	14,2±0,7	11,4±0,3	10,5±0,5	14,2±0,5	16,3±0,6
	0,6	17,9±0,8	14,9±0,5	12,3±0,4	17,3±0,6	22,3±0,8
	1,0	20,8±0,9	17,2±0,6	14,3±0,6	20,5±0,9	24,1±0,9
Chloramine B	1	0	0	0	0	0
Catamine AB	3	15,2±0,5	18,4±0,8	12,5±0,5	20,3±0,7	20,1±0,6
Control (untreated yarns)	–	0	0	0	0	0

* Developed by the authors

Table 4. Antibacterial properties of nonwoven polyamide NFA-containing materials*

Test portions of nonwoven PCA material (fiber fineness, tex)	Concentration of NFA, %	Diameter of the bacterial growth inhibition zone, d, mm				
		Bacillus subtilis	Pseudomonas fluorescens	Erwinia herbicola	Bacillus megatherium	Bacillus mesentericus
No.1 (0,7)	0,2	23,3±0,5	21,8±0,5	15,3±0,8	26,4±0,6	26,9±0,6
	0,6	25,5±1,0	23,2±0,4	17,7±0,3	27,2±0,5	28,3±0,5
	1,0	26,2±0,5	23,7±0,9	18,3±0,7	29,1±0,8	29,8±0,9
Control	0	0	0	0	0	0
No.2 (0,3)	0,2	30,3±0,8	22,9±0,6	19,0±0,2	31,3±0,6	33,8±0,7
	0,6	32,3±0,6	24,2±0,4	21,4±0,4	33,1±0,3	36,5±0,5
	1,0	32,9±0,7	25,0±1,2	22,0±0,7	33,9±0,8	37,0±0,9
Control	0	0	0	0	0	0

* Developed by the authors

36, Bacillus mesentericus 3, Bacillus megatherium 6, Pseudomonas fluorescens 32, Erwinia herbicola 62.

Fungicidal properties of the materials were evaluated by the action of the obtained test portions on the standard set of microscopic fungi (GOST 9.049-91, 1991): *Aspergillus niger van Tieghem, Aspergillus terreus Thom, Aureobasidium pullulans* (*de Bary*) *Arnaud, Paecilomyces variotii Bainier, Penicillium funiculosum Thom, Penicillium ochro-chloron Biourge, Scopulariopsis brevicaulis Bainier, Trichoderma viride Pers*. *ex S.F. Gray*.

For the quantitative assessment of antimicrobial action of the materials treated with biocides, the authors used the technique based on the direct action of these materials on live cells growing on the nutrient medium. The test portions under study – yarns at the quantity of 0,5 mg rolled up in 10 mm diameter balls and nonwoven materials in the form of 10 mm diameter disks – were placed on the surface of agar plates into Petri dishes inoculated with bacteria and the standard set of microscopic fungi. The dishes were kept in the incubator for 24 hours at the temperature of 37^0C (for bacteria) and 30^0C (for fungi). Antimicrobial activity was identified according to the size of sterile zones formed around test portions (Khaliullina & Gadelshina, 2014; Kiselev & Dashchenko, 2020; Kryazhev et al., 2013).

RESULTS AND DISCUSSION

Antimicrobial properties of PCA yarns after treatment with chloramine B, catamine AB, and nitrofuryl-acrolein were studied by measuring the size of sterile zones around test portions of the yarns. Findings of the study of antibacterial action of the yarns are shown in **Table 3**.

The obtained data give evidence about yarns treated with chloramine B having no antibacterial properties. Yarns containing Catamine AB have high indicators of antibacterial action: the bacterial growth inhibition zones range from 12,5 to 20,3 mm.

Yarns chemically modified with NFA have a high antibacterial activity, too, and it is greatest at the concentration of 1%. So, as for their action on the Erwinia herbicola bacteria, the bacterial growth inhibition zone amounts to 14,3 mm, while it is 24,1 mm when acting on the Bacillus mesentericus bacteria. These results confirm that yarns modified with NFA feature a quite high antibacterial activity.

As follows from the obtained data, as the concentration of NFA on fibers and yarns is increased for all the microorganisms included into the scope of study, the bacterial growth inhibition zones are increased, too.

When analyzing the results, the following regularities have been found. The obtained materials had the smallest antibacterial action against the Erwinia herbicola bacteria, and the greatest – against the Bacillus mesentericus ones. Higher resistance to the action of NFA was demonstrated by gram-negative bacteria, and lower – by the gram-positive ones.

The authors also treated two kinds of needled nonwoven polyamide materials with NFA: No. 1 having the surface density of 535 g/m^2 (0,7 tex fiber fineness) and No. 2 having the surface density of 250 g/m^2 (0,3 tex fiber fineness).

Results of studying the action of these fabrics modified with NFA at different concentrations on the bacteria adopted as test cultures are presented in **Table 4**.

The obtained data confirm the high sensitivity of the bacteria used as test cultures to the action of nonwoven materials treated with NFA. Test portion No. 2 (250 g/m^2 surface density, 0,3 tex fiber fineness) has a greater extent of antibacterial action than test portion No. 1 (535 g/m^2 surface density, 0,7 tex fiber fineness). Lower fiber

Table 5. Dimensions of the fungicidal action zone for nonwoven materials containing NFA (standard microscopic fungi set)*

Test portion	Concentration NFA, %	Diameter of the fungicidal action zone, mm	
		after 2 days of action	after 8 days of action
Needled fabric, 535 g/m^2 surface density	0,6	39,0±0,5	18,1±0,2 (32,0 – asporogenous mycelium)
Control	0	0	0
Needled fabric, 250 g/m^2 surface density	0,6	39,0±0,4	18,3±0,3 (32,0 – asporogenous mycelium)
Control	0	0	0

* Developed by the authors

fineness and lower surface density of the material appears to improve adsorption and fixation of nitrofuryl-acrolein on fibers.

The greatest resistance to the action of NFA was demonstrated by the Erwinia herbicola bacteria, which is in line with results of evaluating antibacterial properties of the Letilan fiber (PVAL fiber modified with NFA) against this test culture (Volf, 1980).

Notably, the action of NFA on gram-positive and gram-negative bacteria is not similar.

NFA-containing nonwoven polyamide materials have a greater antimicrobial activity against gram-positive bacteria. So, under the action of material No. 2 (250 g/m^2, 0,3 tex) at the concentration of 0,6%, the diameter of sterile zones ranges from 21,4 to 24,9 mm in gram-negative bacteria, and from 32,3 to 36,4 mm – in the gram-positive ones.

As follows from the data obtained, as the concentration of NFA on fibers and yarns is increased for all microorganisms included into the study, the growth inhibition zone are increased, too.

When analyzing the results, the already registered regularities have been found: the obtained materials had the smallest antibacterial action against the Erwinia herbicola bacteria, and the greatest one – against Bacillus mesentericus. Higher resistance to the action of NFA was demonstrated by gram-negative bacteria, lower – by the gram-positive ones.

Obtained by the authors nonwoven materials produced by the method of needle punching and having NFA in their composition were tested for fungicidal action of the materials against the set of microscopic fungi after 2 and 8 days of exposure, according to the standard technique. Findings of the studies conducted are given in **Table 5**.

Analysis of the results of studying fungicidal properties of the NFA-containing nonwoven materials has allowed classing the needled polyamide fabrics among materials having a high extent of fungicidal action. So, after two days of exposure, these fabrics had the fungicidal action zone diameter equal to 39,0 mm; in 8 days, the diameter of the zone was 2 times smaller; however, asporogenous mycelium was observed around the test portions, which gives evidence about fungistatic action of these materials.

CONCLUSION

Thus, chemical modification of polycaproamide yarns and nonwoven materials with nitrofuryl-acrolein has been conducted.

It is shown that the polycaproamide yarns and nonwoven materials chemically modified with NFA which were obtained by the authors have gained antibacterial activity. With regard to this, their antibacterial activity is higher against gram-positive bacteria and lower against the gram-negative ones.

It has been found that nonwoven materials containing NFA feature a high extent of fungicidal action. It can be said these materials have a fungistatic effect over time.

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