https://doi.org/10.15407/scine17.03.056

MARTIROSYAN, I. A. 1 (https://orcid.org/0000-0003-3733-3004), PAKHOLIUK, E. V.² (http://orcid.org/0000-0002-3484-0468), LUBENETS, V. I.3 (https://orcid.org/0000-0001-6189-0084), KOMAROVSKA-POROKHNYAVETS, O. Z.3 (https://orcid.org/0000-0003-2439-481X), MONKA, N. Ja.³ (https://orcid.org/0000-0002-4373-2987), NAKONECHNA, A. V.3 (https://orcid.org/0000-0003-3539-0160), PEREDRIY, O. I.² (http://orcid.org/0000-0002-5464-2020), and LUTSKOVA, V. I. (https://orcid.org/0000-0002-8965-4224), ¹Odesa National Academy of Food Technologies, 112, Kanatnaya St., Odesa, 65023, Ukraine, +380 48 712 4088, postmaster@onaft.edu.ua ²Lutsk National Technical University, 29, S. Kovalevska Ave., Lutsk, 43008, Ukraine, +380 33 274 6111, pk@Intu.edu.ua 3 National University Lviv Polytechnic, 2, St. Jura Sq., Lviv, 79013, Ukraine, +380 32 258 2111, coffice@lpnu.ua

INNOVATIVE APPROACH TO THE CREATION OF TEXTILE MATERIALS WITH ANTIMICROBIAL PROPERTIES

Introduction. In recent years, there has been a constant search for more advanced and environmentally friendly means for antimicrobial treatment of cellulose-containing tissues of various intended uses in the textile industry.

Problem Statement. The problem of protection of textile materials and products from microbiological de-

struction is complex and multifaceted and needs to be solved. Today, one of the methods of protection is to provide textile materials with biocidal properties, which not only prevents the growth of bacteria, but can also ensure a high level of tissue safety. Therefore, we are faced with the task of finding new safe biocidal products.

Purpose. The research has been made to determine the level of safety of textile materials treated by biocidal substances with the thiosulfonate structure including Ethylthiosulfanilate, Methylthiosulfanilate and Allylthiosulfanilate.

Materials and Methods. The fabrics of different chemical composition were used in the study, designed for the manufacture of overalls. New preparations of thiosulfonate structure were chosen for impregnation: ethylthiosulfanilate (ETS), methylthiosulfanilate (MTS) and allylthiosulfanilate (ATS). The presence of heavy metals and pesticides was determined by atomic absorption spectrometry with the use of a ZEENIT 650P spectrometer (Germany).

Results. It has been established that the detected level of heavy metals and pesticides in the studied textile materials is insignificant and is within the regulatory requirements. It has been confirmed that the studied biocidal substances are low-toxic and environmentally friendly, because before and after treatment they did not change

Citation: Martirosyan, I. A., Pakholiuk, E. V., Lubenets, V. I., Komarovska-Porokhnyavets, O. Z., Monka, N. Ja., Nakonechna, A. V., Peredriy, O. I., and Lutskova, V. I. Innovative Approach to the Creation of Textile Materials with Antimicrobial Properties. *Sci. innov.* 2021. V. 17, no. 3. P. 56—66. https://doi.org/10.15407/scine17.03.056

the hygienic parameters of tissues. A method for imparting biocidal properties to textile materials for the manufacture of overalls, in particular by impregnating textile materials with an alcoholic solution of biocidal products, has been developed. Also due to this treatment, the water absorption of materials decreases by an average of 40%.

Conclusions. The treatment of textile materials with biocidal preparations of the thiosulfonate structure allows obtaining simultaneously two desired effects for these fabrics: the appropriate bioresistance and water resistance.

Keywords: environmental responsible, heavy metals, biocides, hygienic properties, and thiosulfonates.

In recent years, textile industry specialists have been paying attention to the problem of determining the level of environmental responsible and hygiene of clothing and other types of textile materials. Until recently, the demands of consumers and producers of textiles have been related to fashion, shape stability, ease of care and low cost. The negative influence of the textile material was not discussed or discussed last of all.

However, publications on the negative effects of textiles on the human body are appearing increasingly in the world scholarly research literature, also great attention is paid to textile materials with antimicrobial properties because textiles can contribute to the transmission of pathogens [1—6].

In particular, the issue about the development of antimicrobial fibers has been consider by the textile industry since 1941 (Hirschmann and Robinson 1941).

In [1], it is shown the possibility of survival of 60 bacteria strains including four species (*Klebsiella pneumoniae*, *Acinetobacter baumannii*, *Staphylococcus aureus*, and *Enterococcus faecium*) on untreated cotton textiles in clinically significant incubation periods. The antibacterial efficacy of the textiles treated with *Sanitized T99-19* and *Sanitized T27-22*, which contain quaternary ammonium salts (QAC) has been established. The mentioned samples have shown a high influence on the action of bacterial test cultures of the most of grampositive pathogens and ineffectiveness against multiresistant gram-negative bacteria (*Escherichia coli*) [2].

As is known, organic antimicrobial reagents of both natural (chitosan, cyclodextrins and natural dyes) and synthetic origin (various Quaternary ammonium salts, triclosan, halogenated phenols and organometallic compounds) are used for the processing of cellulose textiles. The interaction between cellulose and antimicrobial reagents, mechanisms of their biological action and the influence of various factors on the biocidal activity of textile carriers are illustrated by researchers in the work [3]. In order to improve durability and mechanical properties of textiles it is need to conduct a preliminary activation of its cellulose component or to use linker agents. As antimicrobial agents it is advisable to use environmentally friendly compounds of prolonged action, in particular resistant to hygienic care [3].

The effect of biocides 3-methylol-2,2,5,5-te-tramethylimidazolidinone (MTMIO) and 1,3-dimethylol-5,5-dimethylhydantoin (DMDMH) and their compositions in various ratios for chemical modifications of cellulose was studied by Californian researchers. The use of such compositions for cellulose treatment improves the strength and stability of biocidal functions of tissues treated with these preparations, in addition, these tissues can withstand repeated washing and long shelf life [4].

Another achievement in this direction is cyclodextrins, which are widely used for tissue processing, because due to their unique chemical structure they exhibit the good absorption capacity, namely, they form inclusion complexes with different antimicrobial and other biologically active substances. Therefore, this is undoubtedly important to provide textiles with antimicrobial properties in further studies [5, 6].

Many compounds with a wide spectrum of antimicrobial attributes, high bactericidal and fungicidal activity [7] have been found among thiosulfonates of the general formula RSO₂SR', which are close to structural analogues of natural phytoncides including garlic *Allium sativum*, *Allium*

cepa onion, various types of cabbage, especially cauliflower [8, 9].

The synthetic thiosulfonic acid esters are known to exhibit a wide range of biological activity, which often exceeds the efficiency of natural analogues. Some of them are offered as effective antifungal substances, promising perspective substances of another direction, preservatives of fruits and vegetables, effective remedies for plants, growth regulators, biocidal additives and insecticides. Esters of thiosulfonic acids are effective sulfenylating reagents in organic synthesis, having valuable properties for solving the complex problems of molecular biology and biochemistry [7, 10—11].

But today, the searching of the new environmental ways for providing antimicrobial properties to textile materials does not lose its relevance, despite the existence of numerous studies in this field.

The textile materials can be a source of negative effects of chemicals complex during production. For example, dyes, compounds, and preparations containing heavy metals are used to decorate and provide textiles with specific properties. Their application not only reduces the level of environmental friendliness of the product, but also adverselv affects the environment. These substances can be complex multi-component systems, which are not always completely removed from products and materials at different stages of the technological process. During the operation of clothing under the influence of various factors products of destruction can be also released into the clothing space, which in turn adversely affects the human body, causing various biological effects [12, 13].

All over the world, much attention is paid to the development of various methods for obtaining and studying the antimicrobial properties of textile materials and their safety. Therefore, the issue of creating environmentally friendly textile materials with antimicrobial properties resistant to wet treatments, washing, and solar insolation when the textiles are used in real conditions [14—16], remains quite relevant. Given these facts, it

is obvious that textile products require a great attention to quality and safety.

In Ukraine, ecological safety of textile products is defined in the framework of the draft CMU Resolution on *Approval of the Technical Regulation on Environmental Criteria for the Eco-labeling of Textile Products* as strategic directions and tasks for the implementation of state policy in the field of environmental protection, preservation of the health of the state population.

Also, in 2013, the State Sanitary norms and rules "Textile, leather and fur materials and products" came into force. The basic hygiene requirements were developed for harmonization of domestic standards with the standards of the International Association for Research and Testing in the field of Textile Ecology (OECO-TEX).

The basic hygiene requirements are divided into groups:

- rationing of chemicals in products;
- rationing of indicators such as hygroscopicity, air permeability, specific surface electric resistance and pH level;
- ◆ normalization of harmful substances and their migration from the products into the human body and the environment (the content of free formaldehyde and formaldehyde which is able to partially excrete, residues of heavy metals able to extract, pesticide content, the content of pentachlorophenol, azo dyes and organochlorine carriers, the presence of odor, etc.) [16].

The natural fiber fabrics provide excellent conditions for the development and growth of microorganisms through the ability to retain moisture and microbial enzymes that can easily hydrolyze polymer bonds. Cellulose is known throughout the world as the most common, renewable and almost inexhaustible polymeric material with an exciting chemical structure and properties. Consequently, cellulose polymer is characterized by its chirality, high functionality, biodegradation, the ability to broadly chemical modification and the formation of universal semi-crystalline fibers. Therefore, the functionalization of cellulose textiles is the aim of researchers [15—18].

NHCOR NCOR NH₂ NH₂

Na₂S Na₂S Na SO₂SNa SO₂SNa SO₂SR¹
1 (a, b) 2 (a, b) 3 4 (a-c)

$$R^{1} = CH_{3}(a), CCH_{3}(b), C_{3}H_{5}(c)$$

Fig. 1. The synthesis of used thiosulfonates

Consequently, the study of environmental safety of cellulosic textile materials with antimicrobial properties, obtaining new data on the protective properties of such materials, expanding their scope of application used to be urgent scientific tasks with a great practical importance.

The need of development of new biocidal materials with antimicrobial properties is caused by the changing general biological resistance of the human body. Studies show that there are new types of microorganisms which are resistant to most antimicrobial agents. Also pathways, modes of transmission and the duration of their lives are changing [11, 12, 19—21].

The purpose of the research is to develop the antimicrobial textile materials with the use of biocide compounds of the thiosulfonate structure such as Ethylthiosulfanilate (ETS), Allythiosulfanilate (ATS), Methylthiosulfanilate (MTS) preparations, study their properties and environmental safety in order to use it in seaports and docks. These biocidal preparations are tested and effectively used as biocides to protect paintwork materials, component of anticorrosive composition for pipelines of circulating water supply systems, petroleum products, building materials and constructions, algaecides for surface protection, pac-

kaging materials, for sterilization of culture fluid in biotechnological manufactures [22–23]. To our knowledge ETS, MTS, ATS preparations were used firstly to produce environmentally friendly fabrics according to international indices of safety.

Collection of textiles. The object of our research was cotton and cotton polyester fabrics produced by Toctals Fabrics and Ten Cate Protect, respectively (Table 1). All samples of fabrics are treated by the new species of biocidal preparations possessing thiosulfonate structure, which plays an important role in ensuring safe working conditions in various industries, as well as in seaports and docks. The main functions of such clothes are the preservation of human health, the creation of favorable conditions for high working efficiency in aggressive conditions, protection against the negative influence of the environment, fungal and bacterial microflora.

The biocide preparations. To protect cellulose-containing textile materials and clothing products from the negative effects of fiber-destroying and pathogenic microorganisms, we selected new biocidal preparations having the thiosulfonate structure: Ethylthiosulfanilate (ETS), Allylthiosulfanilate (ATS), Methylthiosulfanilate (MTS), which exhibit a wide spectrum of antimicrobial activity,

Table 1. Properties of the Studied Textile Materials

Sample	Surface Fibrous composition, % density,		Density, <i>P</i> , the number of threads per 10 cm		Linear density of threads, <i>T, tex</i>		Type of coloring	
number		g/m²	Warp	Weft	Warp	Weft		
1	Cotton, 100	245	307	292	49	38	smooth-dyed	
2	Cotton-polyester, 50/50	245	292	220	42	25	smooth-dyed	

are non-toxic, and can be used for antimicrobial protection in various industries.

These thiosulfonates are synthesized at the Department of Technology of Biologically Active Compounds, Pharmacy and Biotechnology in the Lviv Polytechnic National University in accordance with Fig. 1 [22, 23].

Indicators of the minimum concentration of thiosulfonate biocidal preparations for fungicidal (A) and fungistatic (B) treatment of cotton-polyester cloths for their protection against biodestruction by fibrous and pathogenic microorganisms are presented in Table 2.

Methods. In order to determine the environmental quality of textile materials treated with biocidal preparations content of toxic substances, heavy metals, pesticides, measurements have been made at the Kovalevsky Institute of Biology of the Southern Seas of the NAS of Ukraine (Odesa) and at the laboratory of chemical analytical research of the Ukrainian R&D Center of Ecology (Odesa) under the Ministry of Ecology and Natural Resources of Ukraine.

Antimicrobial treatment of cotton-polyester cloths was carried out at the Analytical and Research Testing Laboratory *Textile-TEST*, Kyiv (Kyiv National University of Technology and Design). Samples of tissues were treated by water alcoholic solution (60/40) of ETS, MTS and ATS preparations in padding dyer at room temperature (18–20 °C) and relative humidity of the air 63–65%. Subsequently, these test specimens were pressed with the use of padding dyer to a residual mois-

ture content of 6—8% and dried at 75, 60 and 50 °C. The minimum concentration of ETS, MTS and ATS in water alcoholic solutions was 0.5%. Before all determinations of textile quality, fabric samples were being dried for 5—7 min.

The concentrations of heavy metals were detected by atomic absorption spectrometry (AAS) with the help of spectrometer *ZEENIT 650P* (*Analytik Jena AG*, Germany) including separation/preconcentration procedures, solid phase extraction and coprecipitation. The principle of the spectrometer functionality was based on atomization of the test sample, measuring the optical density of the atomic vapor and further determining the mass concentration of the elements to be determined with the use of calibration curves. All chemicals were purchased in Merck (Darmstadt, Germany).

Another way of detection of heavy metals in textiles was Wet Digestion Procedure (WDP) described by Sungur Ş. and Gülmez F. [24] with the help of MP-AES Analysis. The method was provided by *Agilent 4200 MP-AES (Agilent Technologies*, USA).

The pesticide content and the toxic substances are determined with the help of *Agilent 4200 MP-AES* (*Agilent Technologies*, USA). Also a detector was used to capture electrons (a temperature rise of 1.2 °C per min). The content of organic solvents (benzene, toluene, and xylene) was determined based on the equilibrium concentration of the vapor phase.

The odor intensity of fabrics was determined by 6 experts at the laboratory of sensory analysis in the Odesa National Academy of Food Techno-

Table 2. Minimum Concentration of Thiosulfonate Preparations for Fungicidal (A) and Fungistatic (B) Treatment of Cotton-Polyester Fabrics

	Minimum concentration, %							
Country	ETS		MTS		ATS			
	A	В	A	В	A	В		
Trichoderma viride	0.055	0.006	0.055	0.012	0.025	0.012		
Aspergillus niger	0.055	0.0185	0.05	0.008	0.05	0.008		
Penicillium funiculosum	0.0185	0.006	0.0185	0.006	0.0185	0.006		
Paecilomyces variotii	0.0185	0.006	0.0625	0.003	0.625	0.003		
Chaetomium globosum	0.055	0.006	0.055	0.006	0.12	0.03		

logies. The intensity of smell is determined based on the five-point scale (Table 3).

The chemical research takes into account that the main pollutants are bismuth, cadmium, cobalt, manganese, copper, zinc, nickel, mercury, lead, antimony, chromium, among which lead, mercury and cadmium are global the first class of danger pollutants for the environment. They can remain on the surface or in the structure of textile material, which also affects the human body, causing various biological effects (allergens, skin irritants) with different duration of action and the time of detection [25]. The heavy metals can accumulate in bones and various organs, causing their dysfunction. They can also help to eliminate the beneficial elements from the organism such as magnesium, calcium and others. High concentration of heavy metals in the organism can lead to the following diseases: cancer, acute and chronic renal insufficiency, autism, fetal death, cardiovascular and nervous system diseases, metabolic disorders [30].

In addition, raw materials and products of natural origin are treated with fungicides and insecticides against the destructive action of microorganisms, moths, rodents during storage of textile materials and clothing in warehouses and transportation. Moreover, the heavy metals have particular hygienic significance which can also contaminate textile materials and clothing as a result of the use of dyes, the specifics of technological

Table 3. Odor Scale

Score	Patents in n
0	absent odor that is not detected by any expert
1	barely noticeable odor that is detected by experts having the most sensitive organs of senses
2	faint odor that is detected by experts if they aimed at its definition
3	pronounced odor that is detected by experts if they do not pay attention to it
4	powerful odor that is detected by experts easily
5	heavy odor that is detected by experts without smelling

processes, due to contamination of the ecosystem [27]. The content of heavy metals in fabrics determined with the help of WDP is presented in Table 4.

Copper (26.3—26.4 mg kg⁻¹) was detected in the highest concentrations in cotton-polyester fabrics (Samples No. 2). Also higher content of Chromium (1.29—1.30 mg kg⁻¹) was determined in all cotton-polyester textiles in comparison to samples of cotton fabrics. The levels of Arsenic and Mercury were found to be considerably less than the values demanded by *Oeko-Tex*. However, all concentrations of heavy metals in extract of 0.07M HCL were determined to be within the normal limits.

The content of heavy metals in the studied fabrics measured with the use of AAS is shown in Table 5.

Table 4. Effect of Biocide Treatment on the Presence of Heavy Metals in Fabrics

	Requirements of <i>Oeko-Tex</i> <i>Standard</i> [28], at most, µg kg ⁻¹	Metal content, μg kg ⁻¹							
Metals		Sample №1				Sample №2			
		Without treatment	ETS	MTS	ATS	Without treatment	ETS	MTS	ATS
Co (Cobalt)	4.0	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Cr (Chromium)	2.0	0.54	0.535	0.58	0.537	1.30	1.296	1.30	1.29
Cu (Copper)	50.0	8.84	8.84	8.83	8.84	26.3	26.3	26.4	26.4
Ni (Nickel)	4.0	0.38	0.348	0.35	0.348	0.195	0.196	0.195	0.194
Pb (Lead)	1.0	0.41	0.406	0.045	0.406	0.384	0.379	0.384	0.384
Cd (Cadmium)	0.1	0.045	0.045	0.045	0.045	0.070	0.070	0.070	0.070
As (Arsenic)	1.0	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Hg (Mercury)	0.02	< 0.01	< 0.01	< 0.01	< 0.01	<0.01	< 0.01	< 0.01	< 0.01

26.1	Sam	Sample No.1, µg kg ⁻¹				Sample No.2, µg kg ⁻¹			
Metals	Without treatment	ETS	MTS	ATS	Without treatment	ETS	MTS	ATS	
Cr (Chromium)	1.01	1.00	1.00	1.00	1.37	1.37	1.37	1.37	
Cu (Copper)	10.9	10.9	10.89	10.87	40.2	40.2	40.2	40.3	
Ni (Nickel)	0.372	0.371	0.370	0.372	0.5	0.034	0.036	0.036	
Pb (Lead)	0.454	0.454	0.453	0.453	0.416	0.42	0.413	0.416	
Cd (Cadmium)	0.083	0.083	0.082	0.083	0.084	0.086	0.081	0.082	
Hg (Mercury)	0.018	0.017	0.018	0.018	0.012	0.012	0.012	0.012	

Table 5. Total Content of Heavy Metals in the Studied Fabrics

The total content of Copper (40.2–40.3 µg kg⁻¹) in cotton-polyester fabrics (Sample №2) was the highest among another metals as well as concentration of it found in extract of 0.07M HCL. Also in accordance with literature values of heavy metals in different cotton fabrics the less content of Copper was detected, especially: 0.28–0.84 µg kg⁻¹, $0.26-0.78 \text{ µg kg}^{-1}$ [29], $0.05-0.21 \text{ µg kg}^{-1}$ [30]. However, in study [31] concentration of Copper was three times higher in comparison with the results of our research (until 340 µg kg⁻¹). Lead was detected in the less concentration (0.413– 0.454 µg kg⁻¹) in all fabrics of the present research in comparison with the results of another research (1.23–1.83 µg kg⁻¹). In the studied fabrics, all concentrations of other heavy metals (Sample No.1) and No.2) were determined identically, by cont-

Table 6. Influence of Biocide Treatments on the Content of Organochlorine Pesticides

Influence of Biocide Treatments	Requirements of standard [28],	The content of organochlorine pesticides in tissue samples, µg kg ⁻¹			
on the Content of Organochlorine Pesticides	μg kg ⁻¹ , not more	Sample No.1	Sample No.2		
DDT	1.0	<0.1	23.0		
DDD	1.0	0.05	5.6		
DDE	1.0	2.8	< 0.1		
Heptachlor	0.5	7.40	< 0.1		
Lindan (γ-HCH)	1.0	0.28	< 0.1		
(α-НСН)	1.0	< 0.1	< 0.1		
(β-НСН)	1.0	< 0.1	< 0.1		
Dieldrin	0.2	< 0.1	< 0.1		
Aldrin	0.2	<0.1	< 0.1		

rast to ones without treatment. Arsenic and Cobalt contents were not detected according to method of AAS.

According to data shown in Table 4 and 5 the concentrations of heavy metals in the studied textile materials treated by ETS, MTS, and ATS preparations were virtually the same in comparison with samples of fabrics without treatment and met the requirements of international standard. Obtained results proved that biocide preparations are non-toxic and its use in textile industry does not lead to danger to human health or life.

Organochlorine pesticides in textiles. In order to increase yields, in the traditional method of cultivating raw materials for textiles, not only fertilizers, but also large amounts of insecticides are utilized. Approximately 10% of all pesticides used in the world are in cotton-growing areas. Due to active irrigation, these substances penetrate into groundwater, which leads to the risk of contamination for local sources of drinking water and soils. Approximately 10% of them remain in the can-

Table 7. Odors of the Studied Samples of Textile Materials

Type of treatment	Evaluation of samples, scores			
Type of treatment	Sample No.1	Sample No.2		
Without treatment				
ETS	garlic 2 — faint odor of	2 — faint odor of garlic 2 — faint odor of		
MTS	cabbage	cabbage		
ATS		2 — faint odor of garlic and onion		

vas and can lead to the development of skin diseases and allergic reactions.

Influence of biocide treatments on the content of organochlorine pesticides with mean values is presented in Table 6.

Heptachlor was found in the highest concentration (7.40 μ g kg⁻¹) in cotton fabric samples from comparative to ones from cotton-polyester. It is associated with presence of Heptachlor in soil that contributes to its content in cotton plant during growing [30]. Heptachlor is highly effective in controlling insects thereby it is used for plants but now in the lowest concentrations according to statements of Stockholm Convention on Persistent Organic Pollutants. The content of DDE (2,8 μ g kg⁻¹) also was detected higher than standard norm that is associated with agricultural use.

Study of textile odors. After treatment by ETS, MTS and ATS preparations fabrics had special odors. The results of odor studies are presented in Table 7.

All fabric samples differed by the biocide preparation used. The faint odor of garlic is found in textiles treated by ETS preparation, while faint odor of cabbage is reported for textiles treated by MTS

Table 8. Results of Chemical Analysis of Textile Materials on the Presence of Toxic Substances

Tr. :	Requirements	Measured value, μg kg ⁻¹			
Toxic substances	of standard [28], μg kg ⁻¹ , not more	Sample No.1	Sample No.2		
Formaldehyde	0.05	< 0,02	< 0,01		
Hexamethyle-					
nediamine	0.01	not detected	not detected		
Caprolactam	1.0	not detected	not detected		
Propyl alcohol	0.25	not detected	not detected		
Isopropyl alcohol	0.25	not detected	not detected		
Butyl alcohol	0.1	not detected	not detected		
Isobutyl	0.15	not detected	not detected		
alcohol					
Benzene	0.5	not detected	not detected		
Toluene	0.5	not detected	not detected		
Xylene	0.05	not detected	not detected		
Acetone	2.2	not detected	not detected		
1		I			

preparation and faint odor of garlic and onion was a characteristic for textiles treated by ATS.

Toxic substances in textiles. An important characteristic of textile materials is their ecological cleanliness, namely the absence of toxic substances, and, accordingly, the threats to consumers' health. The results of the presence of toxic substances in textile materials for the production of overalls are shown in Table 8.

The content of formaldehyde in the studied textile materials was within the normal limits, and other toxic substances were not detected at all. The concentrations of formaldehyde in Chinese cotton textiles are higher by several times (89.6 μ g kg⁻¹, 72.3 μ g kg⁻¹) in comparison with our values, even for different methods of its determination. Such fact means that using of biocide preparations for textiles is safe to human life.

Study of the hygienic properties of textiles. Hygroscopicity of textile materials is characterized by their ability to adsorb and desorb hygroscopic and capillary moisture during changing of environmental conditions. It is known that hygroscopicity depends on the fiber composition of the product, the structure of the material and the operating conditions of the product. Influence of biocide treatment of studied materials on change of their hygienic properties is presented in Table 9.

The analysis of the obtained results showed that the biocidal treatment of the studied cellu-

Table 9. Effect of Biocide Treatment of Studied Materials on Change in Their Hygienic Properties

No.	Samples	Hygro- scopicity, %	Water Resistance, Pa	Water absorption, %
1	Without treatment	8.5	0	33.7
	ETS	8.5	760	15.6
	MTS	8.4	750	20.9
	ATS	8.4	750	20.5
2	Without treatment	7.0	0	29.7
	ETS	7.2	600	12.3
	MTS	7.0	590	13.5
	ATS	7.0	590	14.2
	Aldrin	0.2	< 0.1	<0.1

losic textile materials leads to increasing of their hygienic parameters associated with keratolytic action and insoluble properties of used preparations. The protective layers are lipophilic, that also prevents the penetration of water. Particularly high effect was achieved in samples of textile materials treating by ETS as made from cotton as well from cotton-polyester.

In general, the results of studies on the provision of antimicrobial properties with new low to-xic biocidal substances of the ETS, MTS and ATS suggest that the treatment with these preparations allows obtaining at the same time two desired effects on these tissues (appropriate bio resistance and water resistance) and improving their environmental safety, in general.

Consequently, according to the results of the research, samples of cotton and cotton-polyester textile materials treated with new types of biocidal preparations met the criteria for human health safety. Also the present study has confirmed that

the biocidal substances of the ETS, MTS and ATS are low-toxic and environmentally safe, because during treatment with them, the hygiene indices of tissues have not changed. In addition, thiosulfonate biocides do not increase the content of heavy metals, pesticides and other toxic substances used in the cultivation of cotton plant and the production of textiles and can be recommended for the provision of antimicrobial properties to textiles.

Further research. In order to improve the method for applying thiosulfonate biocide compounds to textile materials, it is advisable to develop highly stable nanosize water oligomer systems with thiosulfonates [32, 33] as well as to improve the method for providing textile materials with antimicrobial properties and to ensure their stability and durability. The obtained results may be the source data for the development of scientifically substantiated requirements in the production of clothing for special and technical purposes.

REFERENCES

- 1. Hanczvikkel, A., Vig, A., Toth, A. (2019). Survival capability of healthcare-associated, multidrug-resistant bacteria on untreated and on antimicrobial textiles. *Journal of Industrial Textiles*, 48(7), 1113—1135. https://doi.org/10.1177/1528083718754901
- 2. Borkow, G., Gabbay, J. (2008). Biocidal textiles can help fight nosocomial infections. *Medical Hypotheses*, 70(5), 990—994. https://doi.org/10.1016/j.mehy.2007.08.025
- 3. Emam, H. E. (2019). Antimicrobial cellulosic textiles based on organic compounds. J. 3 Biotech, 9(1), 29—35. https://doi.org/10.1007/s13205-018-1562-y
- 4. Qian, L., Sun, G. (2004). Durable and Regenerable Antimicrobial Textiles: Improving Efficacy and Durability of Biocidal Functions. *Journal of Applied Polymer Science*, 91(4), 2588—2593. https://doi.org/10.1002/app.13428
- 5. Singh, N., Sahu, O. (2019). Sustainable cyclodextrin in textile Applications. *The Impact and Prospects of Green Chemistry for Textile Technology. Woodhead Publishing*, 83, 83–105. https://doi.org/10.1016/B978-0-08-102491-1.00004-6
- 6. Perelshtein, I., Perkas, N., Gedanken, A. (2019). The sonochemical functionalization of textiles. *The Impact and Prospects of Green Chemistry for Textile Technology*. The Textile Institute Book Series, 161—198. https://doi.org/10.1016/B978-0-08-102491-1.00007-1
- 7. Lubenets, V., Stadnytska, N., Baranovych, D., Vasylyuk, S., Karpenko, O., Havryliak, V. Novikov, V. (2019). Thiosulfonates: the Prospective Substances against Fungal Infections. IntechOpen, the world's leading publisher of Open Access books. *Fungal Infections*, 1—25. http://dx.doi.org/10.5772/intechopen.84436
- 8. Nakamura, Y., Matsuo, T., Shimoi, K., Nakamura, Y., Tomita, I. (1993). S-methyl methanethiosulfonate, a new antimutagenic compound isolated from *Brassica oleracea* L. var. *Botrytis. Biological & Pharmaceutical Bulletin*, 16(2), 207—209. https://doi.org/10.5772/intechopen.84436
- 9. Benkeblia, N., Lanzott, V. (2007). Allium thiosulfinates: Chemistry, biological properties and their potential utilization in food preservation. *Food Global Science Book*, 1(2), 193—201.
- 10. Lubenets, V. I. (2003). Thiosulphonic acids derivatives: synthesis and properties. *Ukrainian Chemistry Journal*, 69(3), 109–117 [in Ukrainian].

- 11. Lubenets, V., Luzhetska-Shved, V., Komarovskaya, O., Novikov, V., Kucherenko, L., Smirnov, V., Tolmacheva R. (1999). Antimicrobial Properties of Bioactive Polymers with Thiolsulfonate Fragments. *J. Physiologically active substances*, 2(28), 101–106 [in Ukrainian].
- 12. Galik, I. S., Semak, B. D. (2014). Problems of formation and evaluation of ecological safety of textiles. Lviv [in Ukrainian].
- 13. Pakholiuk, O. V., Martirosyan, I. A. Lubenets, V. I. (2018). The influence of biocidal treatment of cellulose-containing textile materials on the change of their properties. *J. Herald of Khmelnytskyi national university,* 6, 94–98 [in Ukrainian].
- 14. Krichevsky, G. E. (2006). Danger and safety of textile products. J Textile industry, 3, 42-45 (2006) [in Russian]
- 15. Polishchuk, L. V., Kalashnik, O. V., Kirichenko, O. V. (2016). Investigation of the hygiene and safety indicators of baby textiles. *J. Technologies of the food, light and chemical industry*, 5(3), 32–38 [in Ukrainian].
- 16. Ilić, V., Šaponjić, Z., Vodnik, V., Potkonjak, B., Jovančić, P., Nedeljković, J., Radetić, M. (2009). The influence of silver content on antimicrobial activity and color of cottonfabrics functionalized with Ag nanoparticles. *J. Carbohydrate Polymers*, 78(3), 564–569.
- 17. El-Rafie, M., Ahmed, H. B., Zahran, M. K. (2014). Characterization of nanosilver coated cotton fabrics and evaluation of its antibacterial efficacy. *J. Carbohydrate polymers*, 107, 174—181.
- 18. Emam, H. E., Manian, A. P., Široká, B., Duelli, H., Redl, B. Pipal, A., Bechtold T. (2013). Treatments to impart antimicrobial activity to clothing and householdcellulosic-textiles e why "Nano-silver? *J. Clean Prod.*, 39, 17–23.
- 19. Qing, X., Xiating, K., Naiqin, G., Liwen, S., Yanyan, Zh., Feiya, F., Xiangdong, L. (2018). Preparation of copper nanoparticles coated cotton fabrics with durable antibacterial properties. *J. Fibers and Polymers*, 19(5), 1004—1013.
- 20. Martirosyan, I. A., Pakholiuk, O. V. (2018). Environmental safety of new biocidal productsio. *International Multidisci*plinary Conference «Science and Technology of the Present Time: Priority Development Directions of Ukraine and Poland» (October 19—20, 2018 Wolomin, Republic of Poland). 1, 69—71 [in Ukrainian].
- 21. Martirosyan, I., Pakholiuk, E., Lubenets, V., Peredriy, O. (2018). Investigation on stability of textile materials for overalls processed by new biocidal preparation. *Technological Complexes. Scientific journal.* 1(15), 52–59.
- 22. Martirosyan, I., Pakholiuk, E. (2018). Ecological safety of textile materials for the production of overalls. *Materials of the international scientific and practical conference of the applicants of higher education and young scientists "Youth Science and Production"*. *Innovative Technologies of Light Industry"* (May 17—18, 2018, Kherson), 107—109 [in Ukrainian].
- 23. Pylypets, A. Z., Iskra, R. Ya., Havryliak, V. V., Nakonechna, A. V., Novikov, V. P., Lubenets, V. I. (2017). Effects of thiosulfonates on the lipid composition of tissues. *Ukr. Biochem. J.*, 89(6), 56—62.
- 24. Lubenets, V. I., Havryliak, V. V., Pylypets, A. Z.. Nakonechna, A. V. (2018). Changes in the spectrum of proteins and phospholipids in tissues of rats exposed to thiosulfanilates. *Regulatory mechanisms in biosystems*, 9(4), 52–59.
- 25. Sungur, Ş, Gülmez, F. (2015). Determination of metal contents of various fibers used in textile industry by MP-AES. *Journal of Spectroscopy*, 15, 42–48, https://doi.org/10.1155/2015/640271
- Qing, X., Yutong, Z., Shenggao, L. (2015). Assessment of heavy metal pollution and human health risk in urban soils of steel industrial city (Anshan), Liaoning, Northeast China. *Ecotox. Environ. Safe*, 120, 377—385. https://doi.org/10.1016/j. ecoenv.2015.06.019
- 27. Kasiri, M. B., Safapour, S. (2014). Natural dyes and antimicrobials for green treatment o textiles. *Environ. Chem. Lett.*, 12(1), 13—18. https://doi.org/10.1007/s10311-013-0426-2
- 28. Textile industry poses environmental hazards. URL: http://www.oecotextiles.com/PDF/textile_industry_hazards.pdf (Last accessed: 15.05.2019).
- 29. Oeko-tex standard. URL: https://www.oeko-tex.com/ru/consumer/consumers_home/consumer home.xhtml (Last accessed: 15.05.2019).
- 30. Perelshtein, I., Perkas, N., Gedanken, A. (2019). The sonochemical functionalization of textiles. *The Impact and Prospects of Green Chemistry for Textile Technology*, 4, 161–198.
- 31. Tuzen, M., Onal, A., Soylak, M. (2008). Determination of trace heavy metals in sone textile products produced in Turkey. *Bull. Chem. Soc. Ethiop.*, 22(3), 379–384.
- 32. Cai, J. A., Chen, G., Qiu, J., Jiang, R., Zeng, F., Zhu, F., Ouyang, G. (2016). Hollow fiber based liquid phase microextraction for the determination of organochlorine pesticides in ecological textiles by gas chromatography—mass spectrometry. *Talanta*, 146, 375—380. https://doi.org/10.1016/j.talanta.2015.08.069
- 33. Shvets, V., Karpenko, O., Novikov, V., Lubenets, V. (2017). Antimicrobial Action of Compositions Based on Thiosulfonates and Biosurfactants on Phytopathogens. *J. Biotechnology and Biotechnics*, 1(1), 109—117. https://doi.org/10.20535/ibb.2017.1.1.112895

Received 30.01.2020 Revised 25.05.2020 Accepted 23.02.2021

```
I. A. Мартиросян<sup>1</sup> (https://orcid.org/0000-0003-3733-3004),
O.B. Пахолюк<sup>2</sup> (https://orcid.org/0000-0002-3484-0468),
В.І. Лубенець<sup>3</sup> (https://orcid.org/0000-0001-6189-0084),
О. 3. Комаровська-Порохнявець<sup>3</sup> (https://orcid.org/0000-0003-2439-481X),
H. Я. Монька<sup>3</sup> (https://orcid.org/0000-0002-4373-2987),
A.B. Наконечна<sup>3</sup> (https://orcid.org/0000-0003-3539-0160),
O. I. Περεδρίŭ<sup>2</sup> (https://orcid.org/0000-0002-5464-2020),
B.I. Луцькова<sup>1</sup> (https://orcid.org/0000-0002-8965-4224)
<sup>1</sup> Одеська національна академія харчових технологій,
 вул. Канатна, 112, Одеса, 65023, Україна,
 +380 48 712 4088, postmaster@onaft.edu.ua
<sup>2</sup>Луцький національний технічний університет
 вул. С. Ковалевської, 29, Луцьк, 43008, Україна,
 +380 33 274 6111, pk@lntu.edu.ua
<sup>3</sup> Національний університет «Львівська Політехніка»
 пл. Св. Юра, Львів, 79013, Україна
```

ІННОВАЦІЙНИЙ ПІДХІД ДО СТВОРЕННЯ ТЕКСТИЛЬНИХ МАТЕРІАЛІВ З АНТИМІКРОБНИМИ ВЛАСТИВОСТЯМИ

+380 32 258 2111, coffice@lpnu.ua

Вступ. У текстильній промисловості постійно ведеться пошук більш досконалих та екологічних засобів для антимікробної обробки целюлозовмісних тканин різного цільового призначення.

Проблематика. Проблема захисту текстильних матеріалів та виробів від мікробіологічної деструкції складна та багатогранна і потребує рішення. На сьогодні одним із способів захисту є надання текстильним матеріалам біоцидних властивостей, що не тільки запобігає розвитку бактерій, а й може створити високий рівень безпечності тканин. Зважаючи на заначене, постає задача пошуку нових безпечних біоцидних препаратів.

Мета. Визначити рівень безпечності текстильних матеріалів, оброблених біоцидними речовинами тіосульфонатної структури.

Матеріали й методи. Використано тканини різного хімічного складу, що призначені для виготовлення спецодягу. Для просочування було обрано нові препарати тіосульфонатної структури: етилтіосульфанілат (ЕТС), метилтіосульфанілат (МТС) та алілтіосульфанілат (АТС). Наявність важких металів та пестицидів визначали методом атомно-абсорбційної спектрометрії із застосуванням спектрометру ZEENIT 650P (Німеччина).

Результати. Встановлено, що виявлений рівень важких металів та пестицидів у досліджуваних текстильних матеріалах незначний та знаходиться у межах нормативних вимог. Підтверджено, що досліджувані біоцидні речовини є малотоксичними й екологічно безпечними, оскільки до та після обробки ними гігієнічні показники тканин не змінилися. Розроблено спосіб надання біоцидних властивостей текстильним матеріалам для виготовлення спецодягу, зокрема шляхом просочування текстильних матеріалів спиртовим розчином біоцидних препаратів. Також завдяки такій обробці водопоглинання матеріалів знижується в середньому на 40 %.

Висновки. Обробка текстильних матеріалів біоцидними препаратами тіосульфонатної структури дозволяє отримати одночасно два бажані ефекти для цих тканин: біо- та водостійкість.

Ключові слова: екологічна безпека, важкі метали, біоциди, гігієнічні властивості, тіосульфонати.