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**BIOCIDICITY OF PAPER AND BASALT FIBER**

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Today despite the widespread introduction of electronic computer capabilities, paper is still the most widespread media and it's known as a considerable production in the world that is constantly growing. Therefore, the problem of storing paper products is acutely actual. A considerable number of biocides were used to solve this problem, but either the complexity of the use of technology or the danger to the health of staff or the weakness of the drugs – none of the proposed ones did not solve the problem completely and even did not significantly advance its solution significantly. It is simpler and most definitely cheaper to use inorganic fibers, namely basalts, which are characterized by low chemical activity and do not promote the spread of different types of fungi of microorganisms are not subjected to insect mold, etc. During this work samples of paper processed by solutions of disinfection means with prolonged decontamination effect ("Gembar", "Polidese", "Metatin GT") were studied on three types of papers (newspaper, packaging, mucalent). The action biocides was carried out on test cultures of microscopic fungi that were isolated from damaged documents. In addition, samples of paper comprised of compositions of basalt and cellulose fibers, montmorillonite clay and sodium humate (SH) and salts of resin acids (SSRA). Aging samples were observed with indicators such the whiteness of materials the tensile strength (n.d.f.) – properties that are sensitive to the aging process. It is proved in the work that samples that have a composition mixture, basalt fibers almost to the same degree inhibit the spread of fungi and microorganisms as well as typical disinfectants. It was interesting to investigate ether homoionic form montmorillonite which is part of compositions based on basalt and cellulose fibers affect the biocidal characteristic of materials. It has been proven that maximal firming of coagulating systems happens up and adding of 10 % solution of sodium-ion to 15 % suspension of clay. Processing with salts of sodium has a positive impact of behavior of clay mineral of montmorillonite by stimulation creation of firmer composite materials that before. Therefore, the work proposed the material and composition mixture, which guarantees certain physics – mechanical properties and has a much simpler and cheaper technology of obtaining materials.

**Keywords:** biostable material, cellulose, basalt fibers, clay minerals

Today, despite extensive use of electronic computer facilities, paper is still the most widespread storage "device", which is increasingly produced worldwide [1–3].

Storing funds of paper records and preserving historical archive documents require tackling several daunting problems. First of all, premises for storing paper materials must be appropriately organized so that they meet certain requirements: the humidity must not exceed 55–60 % and the temperature must be 15–16 °C; there must not be any mould or microbiological dispersions in the air, etc. Unfortunately, even thorough decontamination does not exclude the necessity of carrying it out again if the conditions are encouraging, which will result in biodeterioration of paper objects. In addition, there appears a problem of coping with the moldy smell, brittleness of leaves and, the most frightful, black mould.

At present, there are a great number of biocides which have been used quite efficiently

for fighting black mould [4]. Many of them were rejected due to complexity of usage or health risks they imposed on the personnel of repositories and visitors [5]. The biocidal substances used were formalin, ammonia liquor, furaciline, thymol, salicylic acid, DDT, etc. Yet neither of them eliminated the problem. Gas-phase treatment of damaged materials with ozone showed good results and, which is essential, was safe for people and environment. The use of ozone, however, expedites ageing [6] and requires complicated conditions. Moreover, it does not eliminate new mould growth [7].

The simplest and less costly solution to the problem is to produce composites containing inorganic fibres, which do not encourage microbial and fungal infestation, are not susceptible to mould, bacteria of different types, insects, vermin, bugs, etc. These fibres are promising composite materials in different respects.

Cardboard-like materials based on basalt fibres (thick felt, tiles, sheets, etc.) are mainly

used as building materials. These materials do not need binders as they contain evenly intertwined fibres of basalt itself. They are usually thick sheets in which coupling between the fibres is solely mechanical. To produce strong paper-like material, different binders are used dependent on the field of application and requirements the products must meet. The most common used binders are cellulose fibres provided the application does not require operation at temperatures higher than 120–130 °C.

The electrokinetic potentials that basalt and cellulose fibres have at the fibre-solution interface the same sign but different values [8]. Recharging the surface of one of the contacting fibres enables one to obtain a material consisting of oppositely charged particles, which increases the strength of the product and its bioresistance.

Our earlier studies showed that clay minerals can be used to obtain a thin, elastic and even heat resistant material, which inhibits the growth of microorganisms considerably [9].

In this work, paper specimens treated with solutions of disinfectants having prolonged biocidal action were studied. The disinfectants under consideration were “Gembar” (from research and manufacturing enterprise «Biocid», Kyiv [10]), “Polidez” (from “ZAT Ukrainian ecological technologies” company, Kyiv [11]) and «Metatin GT» (from Acima company, Switzerland). These three disinfectants belong to

low-toxicity substances (hazard class 4). The paper specimens were immersed in 1.0, 1.5, and 2.0 % solutions of the Gembar, Polidez and Metatin preparations for 4–5 s.

The disinfectants form a polymer film, which can be easily washed out if necessary, on the treated surface therefore provide a prolonged biocidal action.

The effect of the preparations under study on the growth of fungi was investigated using slightly moistened solid medium by the conventional agar well diffusion method in the presence of inhibition zones.

The action of the biocides was studied in test-cultures of microfungi taken from infected paper documents. These microfungi were *Alternaria alternata*, *Aspergillus niger*, *Aspergillus repend*, *Aspergillus ustus*, *Aspergillus versicolor*, *Chaetomium globosum*, *Cladosporium sphaerospermum*, *Paecilomyces variotii*, *Penicillium aurantiogriseum*, *Penicillium tardum*, and *Trichoderma viride*. All of them containate and destroy different materials.

The solutions investigated were 2 % solutions of the Gembar and Polidez preparations and 1 % solution of Metatin. It was found that the effect of the compounds under study on the fungi cultures can be characterized as fungicidal. Table 1 presents data on the effects of the compounds under study on physical-mechanical properties of paper specimens.

**Table 1.** Changes in physical-mechanical properties of newspaper, micalent, and wrapping paper after treatment with biocides

Indicator (newspaper paper)	Before treatment	After treatment with biocides		
		Metatin	Gembar	Polidez
Whiteness,%	62.2	60.4	58.6	58.8
Tensile strength (n.d.f.)	74.2	–	48.4	26.6
Indicator (micalent paper)	Before treatment	After treatment with biocides		
		Metatin	Gembar	Polidez
Whiteness,%	70.6	72.2	72.6	72.0
Tensile strength (n.d.f.)	2476	1276	1036	1472
	(in the machine direction)			
Indicator (wrapping paper)	Before treatment	After treatment with biocides		
Whiteness,%	61	62.2	61.5	61.8
Tensile strength (n.d.f.)	1130	938	784	924

Simultaneously, specimens of paper containing 30 and 50 % basalt fibres (BAS), 70 and 50 % cellulose fibres (CEL), 15 % (with

respect to the fibre weight) montmorillonite clay (MOT), and 10 % (with respect to the fibre weight) of sodium humate (SH) and sodium salts

of resin acids (SSRA) were investigated. Newspaper, micalent and wrapping paper was used as objects of the study.

Ageing of the substrate after treatment with biocides and composites containing basalt fibres were studied using such indicators as whiteness,

folding endurance (n.d.f. is the number of double folds), which are the most important characteristics of paper susceptible to ageing.

Table 2 and Table 3 show physical-mechanical properties of newspaper, micalent and wrapping paper specimens having different compositions.

**Table 2.** Physical-mechanical properties of 30 % (50 %) basalt fibre (BAS) + 70 % (50 %) cellulose fibre (CEL) + 15 % (with respect to the fibre weight) montmorillonite clay (MOT) and 10 % (with respect to the fibre weight) sodium humate (SH)

Composition	Whiteness, %	Tensile strength (n.d.f.)
30 % BAS + 70 % CEL + 15 % MOT + 10 % SH (newspaper paper)	56.2	72.2
30 % BAS + 70 % CEL + 15 % MOT + 10 % SH (micalent paper)	60.4	2270.0*
30 % BAS + 70 % CEL + 15 % MOT + 10 % SH (wrapping paper)	58.6	1068.0
50 % BAS + 50 % CEL + 15 % MOT + 10 % SH (newspaper paper)	60.2	70.0
50 % BAS + 50 % CEL + 15 % MOT + 10 % SH (micalent paper)	58.8	2268.0*
50 % BAS + 50 % CEL + 15 % MOT + 10 % SH (wrapping paper)	56.6	1086.0

\* in machine direction

**Table 3.** Physical-mechanical properties of newspaper, micalent and wrapping paper specimens containing 30 % and 50 % basalt fibre (BAS) + 70 % and 50 % cellulose fibre (CEL) + 15 % (with respect to the fibre weight) montmorillonite clay (MOT) and 10 % (with respect to the fibre weight) sodium salts of resin acids (SSRA)

Composition	Whiteness, %	Tensile strength (n.d.f.)
30 % BAS + 70 % CEL + 15 % MOT + 10 % SSRA (newspaper paper)	58.4	64.6
30 % BAS + 70 % CEL + 15 % MOT + 10 % SSRA (micalent paper)	62.4	2286.0
30 % BAS + 70 % CEL + 15 % MOT + 10 % SSRA (wrapping paper)	60.8	1064.0
50 % BAS + 50 % CEL + 15 % MOT + 10 % SSRA (newspaper paper)	64.4	62.8
50 % BAS + 50 % CEL + 15 % MOT + 10 % SSRA (micalent paper)	66.2	2294.0
50 % BAS + 50 % CEL + 15 % MOT + 10 % SSRA (wrapping paper)	56.8	1082.0

In addition, samples of the same paper (newspaper, micalent, packaging) were studied in parallel. They were treated with composite composition, which included basalt and cellulosic fibers, montmorillonite clay minerals and sodium humate:

a) 30 % basaltic fiber (BAS) + 70 % cellulose (CEL) fiber + 15 % (to weight of fibers) of

montmorillonite clay (MOT) and 10% (to weight of fibers) of humate of sodium (SH);

b) 50 % BAZ + 50 % CEL + 15 % MOT and 10 % SH.

Some compositions had a slightly different composition, namely:

c) 30 % BAS + 70 % CEL, 15 % MOT + 10 % (to weight of fibers) of sodium salts of resin acids (SSRA);

d) 50 % BAS + 50 % CEL + 15 % MOT + 10 % SSRA.

Aging of the mineral basis after treatment with its various biocides was studied by such important properties of papers that are sensitive to the aging process, such as the number of double extremities (strength to breakage and whiteness, given in Tables 2 and 3).

It was interesting to investigate whether the form of montmorillonite, which is part of compositions based on basalt and cellulosic fibers, affects the biocidal characteristics of materials.

It is known that bentonite clays, which include clay mineral montmorillonite, are very hydrophilic, have a relatively high specific surface, a sufficiently complex porous structure and a significant exchange capacity. Dependent on the kind of exchange cations, it is possible to significantly change and adjust the strength properties of the coagulation structures of the clay minerals.

The process included montmorillonite clay from Pizhevsky ancestry. Samples that included

basalt and cellulose fibers, montmorillonite clay of different homoion forms of changeable cations of metals were investigated. The method of getting homoion montmorillonites is described in [10, 11].

It was proven that maximal firming of coagulating systems happens upon adding of 10 %-solution of sodiumion to 15 %-suspension of clay. Little worse results are received from applying salts of calcium, the worst results – from salts of aluminum.

The process included composites of sodium-montmorillonites.

For the sake of comparison, we took the same composition variants of the materials replacing the output montmorillonite with the one processed with salts of sodium. All the data are in Table 4, which shows that processing with salts of sodium has a positive impact on behavior of clay mineral of montmorillonite by stimulating creation of firmer composite materials than before.

**Table 4.** Physical-mechanical properties of papers

Composition	Whiteness, %	Breakage strength and durability (n.d.f.)
30 % BAS+70 % CEL + 15 % Na-MOT + 10 % SSRA Newspaper paper	61.8	66.2
30 % BAS+70 % CEL+ 15 % Na-MOT + 10 % SSRA Micallet paper	64.4	2288.0*
30 % BAS + 70 % CEL + 15 % Na-MOT + 10 % SSRA Package paper	63.6	1067.0
50 % BAS + 50 % CEL + 15 % Na-MOT + 10 % SSRA Newspaper paper	66.6	64.8
50 % BAS + 50 % CEL + 15 % Na-MOT + 10 % SSRA Micallet paper	68.2	2296.4*
50 % BAS + 50 % CEL + 15 % Na-MOT + 10 % SSRA Package paper	58.8	1084.0

\* in machine direction

Table 4 has the information of physical-mechanical properties of newspaper, macallet, and package papers that include 30 % of basalt (Bas) + 70 % cellulose fiber (Cel) + 15 % of Na-montmorillonite (Na-MOT) (in addition to weight of fibers) and 10 % (in addition to weight of fibers) and sodium salts of resinous acids (SSRA) and 50 % of basalt (Bas) + 50 % of cellulose (Cel) + 15 % (in addition to weight of fibers) of Na-montmorillonite (Na-MOT) + 10 % (in addition to weight of fibers) of sodium salt of resin acids (SSRA).

Samples that had sodium humates instead of sodium salts of resinous acids in their composition have almost the same values of whiteness and durability. They are not included into this investigation.

## CONCLUSIONS

1. Data of the investigation provide a possibility to suggest a material and composition that effectively suppresses growth of fungus, moldiness, decreases durability of agglomerate spores, increases resistance.

2. Almost all test materials are destroyed by fungus (destruction by different kinds of fungus of different degrees)
3. Materials that contain more cellulose fibers are affected by fungus more and faster.
4. Biodurability of materials is increasing upon increase of basalt fiber in their composition.

The best values on physical-chemical properties and biodurability are in the compositions that contain basalt and cellulose fibers, Na-montmorillonite clay, humate of sodium (as well as sodium salts of resin acids). Indicators of breaking durability are much higher than in compositions that were processed by previous biocides.

## **Біоцидність паперів та базальтоне волокно**

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*На сьогоднішній день, попри широке впровадження електронних комп'ютерних технологій, папір все ще залишається найбільш розповсюдженим носієм інформації та його виробництво в світі постійно зростає. Тому проблема зберігання паперових виробів є актуальною. Для вирішення цієї проблеми використовувалася велика кількість біоцидів, та складність використання технологій, або небезпека для здоров'я персоналу - жоден з запропонованих не вирішив проблему повністю. Простіше і навіть дешевше використовувати неорганічні волокна, а саме базальти, які характеризуються низькою хімічною активністю і не сприяють поширенню різних видів грибків мікроорганізмів, не піддаються дії комах і т.д. В цій роботі зразки паперу було оброблено розчинами засобів дезінфекції з тривалим дезактиваційним ефектом ("Gembar", "Polidese", "Metatin GT") на трьох типах паперів (газети, упаковка, мукаленти). Дія біоцидів була перевірена на тестових культурах мікроскопічних грибів, які були ізольовані з пошкоджених документів. Крім того, зразки паперу складаються з композицій з базальту та целюлозних волокон, монтморилонітової глини та гумату натрію (SH), та солей смоляних кислот (SSRA). Процес старіння зразків вивчали за такими показниками, як білість матеріалів, міцністю на розрив (n.d.f.). Також було досліджено вплив гомоіонної форми монтморилоніту, що застосовувався в композиціях з базальтовими волокнами, на біоцидні характеристики матеріалів. В роботі доведено, що попередня (до контакту компонентів) обробка солями натрію вихідного застосованого в роботі монтморилоніту позитивно відбилися на глинистому мінералі, що використовували в композиційному складі з базальтових та целюлозних волокон – це стимулювало утворення найбільш міцних композицій. В роботі доведено, що зразки, що мають композиційну суміш з базальтовими волокнами, майже однаково пригнічують розповсюдження грибів та мікроорганізмів, як і типові дезінфікуючі засоби. Тому в роботі пропонується композиційна суміш, яка гарантує певні фізико-механічні властивості і має набагато простішу і дешевшу технологію отримання матеріалів.*

**Ключові слова:** біоцидні матеріали, целюлоза, базальтові волокна, глинисті мінерали

## **Биоцидность бумаг и базальтовое волокно**

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*На сегодняшний день, несмотря на широкое внедрение электронных компьютерных технологий, бумага все ещё остаётся наиболее распространённым носителем информации и её производство в мире постоянно растёт. Поэтому проблема хранения бумажных изделий является актуальной. Для решения этой проблемы использовалась большое количество биоцидов, но, или сложность использования технологий, или опасность для*

здоровья персонала - ни один из предложенных не решил проблему полностью. Проще и даже дешевле использовать неорганические волокна, а именно базальты, которые характеризуются низкой химической активностью и не способствуют распространению различных видов грибов, микроорганизмов, не поддаются воздействию насекомых и т.д. В этой работе образцы бумаги были обработаны растворами средств дезинфекции с длительным дезактивационным эффектом ("Gembar", "Polidese", "Metatin GT») на трех типах бумаг (газеты, упаковка, мукаленты). Действие биоцидов было проверено на тестовых культурах микроскопических грибов, которые были изолированы из поврежденных документов. Кроме того, образцы бумаги состоят из композиций базальта и целлюлозных волокон, монтмориллонитовой глины и гумата натрия (SH), и солей смоляных кислот (SSRA). Процесс старения образцов изучали по таким показателям, как белизна материалов, прочность на разрыв (n.d.f.). Также было исследовано влияние гомоионной формы монтмориллонита, применявшейся в композициях с базальтовыми волокнами, на биоцидные свойства материалов. В работе доказано, что предварительная (до контакта компонентов) обработка солями натрия исходного примененного в работе монтмориллонита положительно отразилась на глинистом минерале, что использовали в композиционном составе из базальтовых и целлюлозных волокон - это стимулировало образование наиболее прочных композиций. В работе доказано, что образцы, имеющие композиционную смесь с базальтовыми волокнами, почти одинаково подавляют распространение грибов и микроорганизмов, как и обычные дезинфицирующие средства. Поэтому в работе предлагается композиционная смесь, которая гарантирует определенные физико-механические свойства и имеет гораздо более простую и дешевую технологию получения материалов.

**Ключевые слова:** биоцидные материалы, целлюлоза, базальтовые волокна, глинистые минералы

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