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FUNGI-RESISTANT BASALT FIBER MATERIAL

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Leading industrial countries display the growth of paper industry even more than other industries. The paper is and was very important for our civilization. Technical industries also require the paper. The electro-technical, radio-technical industries use widely various kinds of paper for the production of things like cables, condensers, radio-diffusers, resistors, TV-sets and so on. In the chemical industry papers are used for chromatography, electrophoresis etc.

But besides of clear advantages for simple usage there are some another advances for some usage namely materials which are resistant to mold fungi and the microorganisms.

It is known that the least subject to the fungi effect are things what are consisted as linen fibers among all as well as sulfite and sulfate cellulose. The artificial fibers are more resistant than natural.

Obviously the problem of conservation of already printed on paper materials growths more and more every year. Now it is strange when we can't read old books which have not being saved in new digital formats. That is why the preserve the old paper literature in worthy state is so important for us and for future generations, and the problem of obtaining so called "biocide" material is so actual. It means such material which may destroy bacteria, mold fungi, and insects. In this work we have used the clays from Zakarpatiyan oblast Horbsky field. These clays are classified as bentonite type and have the following consistence with particular size is between 0,3 and 0,25 mm.

The authors studied the sorption of latexes by basalt fibers. The following latexes were investigated: divinyl methyl methacrylate (DMMA), divinyl nitrile (SKN), isoprene nitrile (L-7). A method was used to recharge the surface of cellulose fibers to obtain a flexible, durable filter material. We checked the resistance of materials to mold.

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

Introduction

Last time we could observe the increasing of the ways for obtaining such kind of materials: injecting biocide materials into paper mass or processing in the gluing press. Besides, everyone agrees that it is inadmissible to use toxic substances in the production of materials for packaging food, medical, cosmetic and other products.

This scientific work is about the new kind of "technical paper", namely the paper which contains basalt fiber. Basalt fiber means inorganic fiber with low chemical activity. That means low compliancy to fungi, microorganisms, insects etc.

This work describes low-cost basalt-fiber based paper-like material with some bonding parts like cellulose, latex etc which is not complicated in production.

There is no problem to obtain carton-like materials based on basalt fibers even without use of binding agents, for example: felt, plates and so on. But if you want to get thin transparent paper-like material you never do without binders. For this, depending on the requirements for the finished product, binders of various types that meet the necessary requirements can be used.

Clay materials have proven themselves well, especially bentonite clays, which are characterized by a pseudo-hexagonal arrangement of silicon oxide tetrahedra, interconnected with each other and capable of forming spatial coagulation structures with water. Bentonites tend to form thixotropic structured systems in suspensions, adsorb gases, liquids and solid compounds on the surface, as well as interact with many substances that regulate their strength and deformation properties.

In the course of work, it was found that for use in combination with basalt fiber, bentonites from the Pyzhevsk mine are best compared to others: Kuntsevo, Cherkassy, Nadeevo [1]

The work shows that the treatment of montmorillonite with an electrolyte peptizer (for example, calcium chloride) contributes to an increase in the formation of coagulation structures with specific structural and mechanical properties. Due to the replacement of calcium ion in suspensions with sodium ion, an increase in plastic strength, stability, and the formation of thixotropic structures are stimulated (maximum strength is observed with the introduction of 0.25% calcium chloride (Table 1).

Table 1. Straightness of materials containing 80% of basalt fiber, 10% of cellulose fiber and 10% of montmorillonite treated by calcium chloride solution

Temperature, ^{o}C	Breaking weight, kgf
20	0,68
120	0,82

Since the basalt and cellulose fibers have equal by sign but different by value electro-kinetic charge one of these fibers (before they contacted each other) we have recharged by aluminium sulfate to get the surface charge to be positive. Thus, as you can see the coupling of two against-charged fibers strengths the final product (Table 3).

Since the electrokinetic charge of basalt and cellulose fibers is the same of sign, but different in value, before the contact of these two fibers, one of them (for example, cellulose fiber) was recharged with aluminum sulfate until the surface charge reversed, i.e. became positive. Thus, the connection of two oppositely charged fibers contributed to the strengthening of the interaction between them, which led to an increase in the strength of the finished product in Table 2.

Table 2. The straightness of materials containing basalt, recharged cellulose fibers as well as 15% of montmorillonite (relatively to fibers mass) processed by suspension of sodium chloride with 10% of NaCl and 1% of calcium chloride

	Contain of cellulose fibers		Montmorillonite treated by:			
			10% NaCl		The suspense of 10% NaCl and 1% of $CaCl_2$	
	Capacity of cellulose fiber					
	25%	40%	25%	40%	25%	40%
Breaking weight, rgn	146	424	168	496	174	522
Breaking length, m	212	826	184	544	186	664

Some troubles occur with the safety of finished products since the human beings are on the Earth. The most of problems concern bacteria, fungi, microorganisms and like that. So, we do have to have so called "biomicide" material to resist them all. Namely, this is a special material which may kill bacteria, mold fungus and insects. The latter are better, however. One of the most important applications for this is packaging materials for various kinds of food. Besides, the paper is got older if the environment is too hot or wet or due to other inappropriate factors. We can improve the situation by invading some biocide materials, but we shall be careful because many of them are toxic and should not be used in general places.

Experimental part

For this work we have used the clays from Zakarpatiyan oblast Horbsky field. These clays are classified as bentonite type and have the following consistence with particular size is between 0,3 and 0,25 mm.

Bentonite clays have relatively high BET specific surface 422 m^2/g as well as hydrophilic properties and porous structure and many other features, all that causes high sorption quality.

To obtain solid and crumb material one have to have the suspension of bentonite in dispersed condition. During the slow boiling of such suspense the particles row over the surface in parallel and create the planted film. For these purposes the Na-bentonite dispersions are good. To obtain the desired suspension it is necessary to remove the electrolyte as completely as possible, because material obtained with too much salt becomes porous and has a low strength. To obtain Na-bentonite, the method of neutralizing the suspension in an acid form with sodium hydroxide is used: bentonite is poured with distilled water in a ratio of 1:10 to swell for three days. The swollen mass was rubbed on a sieve with 4900 holes per cm^2 and diluted five times with 0.05 HCl. After daily sedimentation, the liquid above the precipitate was removed by decantation. The process was repeated until a weak reaction to Ca^{+2} ion (with ammonium oxalate) was obtained.

Excess hydrochloric acid was removed by decantation with distilled water. The bentonite in acid form which we have obtained was then neutralized by means of natrium hydroxide with Ph 8,3 to 8,5. As it was revealed, for the strong foundation for bentonite suspension in acid form the full neutralization does not occurred. Potentiometric investigations have shown that porous structure of montmorillonite depends on the nature of exchange cations.

The cellulose distraction is the complex biochemical process. Mostly it's done by microorganisms with specific ferment – cellulase. There is not a consensus about the cellulose distraction by mold fungi.

In general all tests of cellulose biostability are carried out on pure growth of particular kinds of microorganisms. But as it was demonstrated fungi mix gives better result since inactive fungi together with active ones become significantly active too. Besides, the material is destroyed not only by one kind of fungi, this is the result of fungi mix activity. Compositions which contain basalt fiber expand the zone of growth depression of such types of microorganisms. Previously recharged cellulose fiber has a positive effect on expand the zone of growth depression of fungi and microorganisms.

To make the interaction between basalt and cellulose effective in materials compositions one may use the recharge of one of components' surface because they have the same surface charge by sign but with different with values. Using the fact that surface recharge rates are different it is possible to treat the material by aluminium sulfate without components separation to get an effect of recharge or decreasing one of components' zeta potential almost to zero. It increases the possibility of mutual coagulation of oppositely charged fibers' surfaces (to recharge the cellulose fibers we decrease pH of the solution; if it's necessary to recharge of basalt fibers we increase pH of the suspension).

It was found that by adding the Na-bentonite to the composition the strength of material with rising temperature increases. This may be explained by the fact that single strength contacts between Na-bentonite particles increases as well as increases their contact with basalt fiber surface because rising the temperature exhausts spare and adsorbed water from the system.

Table 3. Breaking weight (kg) depending of temperature

Temperature, ^{0}C	Suggested material	Standard material
20	0,30 to 0,34	
300	0,47 to 1,30	1,20
500	0,58 to 1,52	0,15 to 0,43

Pretty good results of paper-like materials strength were obtained using latexes in composition with basalt and cellulose fibers mix, for example latex-DMMA-65GP, fluorinated latex, latex SKF-260 and latex SKN-40.

Adding the mix of fluorinated latex with Na-bentonite to the blend composition gives the possibility to obtain much more strong filtering material (breaking weight is 1,0 kgf, fracture strength – up to 800 rgn, resistance to air flow – 24 mmWC.

It is possible to apply the natural palygorskite instead of Na-bentonite. Palygorskite is widely used as filtering absorbent due to its corpuscles' comb structure what leads to very good mechanical and thermal stability. Mechanical strength features of the material of the same composition are some higher (Table 4).

Table 4. Breaking weight depending on the temperature

Temperature, ^{0}C	Breaking weight, kg
20	0,500 – 0,600
300	0,670 – 0,720
500	0,780 – 0,840

As one can see admixing bentonite or palygorskite to the composition increases the strength of materials due to formation of pieces rough surface. For temperatures of 1050 – 1100 ^{0}C the strength practically is not changed what could be the result of growth of connected particles quantity.

One of the main problems is the selection of binding component which should bind basalt fibers but does not affect material initial characteristics. For this purpose the bentonite clays are recommended. It is known that the ability of clays to sorb liquid and gas substances on their surface is connected with mineral's surface activity and its textural features, i.e. porous structure. In other words, sorption capacity depends on submicroscopic structure of clay material as well as crystal structure of particles which it consists of. During the processing samples with temperature of 1050 – 1100 ^{0}C the straightness is increasing due to more binding mass formation.

Addition of the cation-active agents to the system (for example electrolytes) leads to their adsorption in Stern layer and therefore decrease of negative charge (the value of potential) of the surface. At a certain concentration of electrolyte (0,1% for aluminum sulfate and up to 0,3% for aminopolyamide relatively to fiber mass) the charge of basalt fibers decreases almost to zero and then, swapping the sign, continue to rise. Increase of positive potential value continues up to certain electrolyte concentration, after that the concentration does not have a significant impact on the potential. Probably Stern layer becomes saturated by electrolyte ions and further increase of electrolyte concentration has only insignificant effect on double electric layer behavior.

When using aluminum sulfate the recharge of basalt fibers surface takes place at pH of 4,95 – 5,05 while for polyelectrolyte this value is a bit higher: 6,0 – 6,1.

The authors have attempted to find a connection between basalt fibers zeta potential changes and their ability of binding matters retention (sorption) such as latexes for example. The sorption of latexes by basalt fibers was investigated by method of Voyutskiy. The method is based on comparison of optical density of latex solutions which do not contain basalt fibers with those ones which have been in the contact with basalt fibers for some time. Sorbent equilibrium in the system of latex – basalt fiber establishes in a few hours. The following latexes were investigated: divinyl methyl methacrylate (DMMA), divinyl nitrile (SKN), isoprene nitrile (L-7). To get more strength there was used the sulfite unbleached cellulose with freeness of 60 ^{o}SR and aluminum sulfate. At pH value of 3,7 – 4,1 the negative charge of cellulose fibers decreases under the influence of aluminum sulfate and changes itself to positive, so the cellulose fibers surface recharge happens resulting in flexible strong filter material. The characteristics are listed in Table 5.

Table 5. Strength and filtering characteristics of the material

Parameter	Output cellulose fiber			Recharged cellulose fiber		
Percentage	90%	50%	20%	90%	50%	20%
Breaking length, m	8340	2415	46	9215	3864	62
Number of double bends	1860	1230	28	2010	1460	42
Air flow resistance, mm WG	10	14	18	22	28	36
Time of free flow, min	1,02	1,06	1,08	0,98	0,94	1,12

The data listed in Table 5 indicate that to obtain the material with advanced features, i.e. to obtain better reaction between fibers of different nature, it is important to recharge one of them having defined their initial surface potential. Such a way gives the possibility to eliminate from the composition expensive imported binding materials such as latex and decrease the content of toxic products in water and air and at the same time obtain better filter material.

The meaningful role in formation of hydration sheath around the particles of dispersion phase belongs to exchange cations. It is known that depending of exchange cations types one may change and regulate clay mineral's structure and strength characteristics. Note that exchange cations activity affects not only the thickness of exchange layer but the quantity of structure-forming particles in volume unit. By values of wetting heat and by amount of bound water the exchange cations can be arranged in a row: $Ca^{+2} > H^{+} > Na^{+} > K^{+}$. Despite the fact that Ca-bentonite binds the water for example half times more than Na-bentonite their thixotropic properties are opposite. In Flyate's opinion [2] Ca-bentonite has the ability to form primary hydrated structures which have stronger bond between particles forming the skeleton than Na-bentonite.

For material compositions we have used Pyzhevsk ball-milled bentonite sifted through a sieve of 900 holes per cm^2 and dried at the temperature of 150 – 200 ^{o}C for 2 hours.

The prime requirement for investigation methods was that samples were put into rough conditions for materials and supportive environment for microorganisms growth [3].

For greater objectivity, the fungus resistance of the materials was tested by three independent methods: in the Van-Iterson's liquid medium (1), on the surface of the agar (Chapek's environment (2) and in the dampening chamber with relative humidity of 98% (3) [4]. Inoculations were valued by 10-score system where 10 meant the highest high degree of fungi overgrowth.

The results of experimental investigations of materials destroying by mold fungi are listed in Table 6.

Table 6. Biostability of materials of various compositions containing basalt fiber (Bas), cellulose fiber (Cel) and montmorillonite (MOT) in different environments: 1 - Van-Iterson's liquid medium, 2 - on the surface of the dewaxed agar (Chapek's environment), 3 - in the dampening chamber

Compositions	Fungi types											
	Chaetomium globosum			Paecilomyces variotii			Stachybotrys atra			Fungi mix		
	Samples biostability test environment											
	1	2	3	1	2	3	1	2	3	1	2	3
50% Bas + 50% Cel	6	6	5	6	5	5	5	5	5	6	6	6
50% Bas + 50% Cel + 15% MOT	4	4	4	4	4	3	4	4	3	4	4	4
70% Bas + 30% Cel + 15% MOT	3	3	3	3	3	3	3	3	2	4	4	4
80% Bas + 20% Cel + 15% MOT	2	2	2	3	2	2	2	2	2	3	3	3

As can be seen from the table, all investigated materials to some extent fall under the action of fungi, are affected and destroyed by them [5].

Conclusions

Materials with a greater amount of cellulose fibers in their composition are affected by fungi to a greater extent and faster. Samples containing up to 85% cellulose fibers are affected by fungi already on the fifth day, and after about ten days the material is completely covered with mold. Materials containing up to 20% cellulose fibers in their composition are more resistant: mold appears only on the fifteenth - seventeenth day.

Biostability increases with an increase the amount of basalt fiber in the composition.

Recharging one of the fibers (changing the surface potential) with aluminum sulfate stimulates the production of a more durable material with better service characteristics.

We would recommend a competent filter-like material, which includes cellulose and basalt fibers, as well as bentonite clay montmorillonite of the Pizhevsky mine. The biostability of such a material is the best.

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ФУНГИЦИДНО УСТОЙЧИВЫЙ МАТЕРИАЛ НА ОСНОВЕ БАЗАЛЬТОВОГО ВОЛОКНА

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Ведущие индустриальные страны демонстрируют рост бумажной промышленности даже больше, чем другие отрасли. Бумага была и была очень важной для нашей цивилизации. Технические отрасли также нуждаются в бумаге. В электротехнической, радиотехнической промышленности широко используются различные виды бумаги для производства таких приборов, как конденсаторы, радиодиффузоры, резисторы, телевизоры, кабели и т. п. В химической промышленности бумага используется для хроматографии, электрофореза и т. д. Но помимо очевидных преимуществ для такого простого использования, есть потребность в материалах, устойчивых к плесневым грибам и микроорганизмам.

Известно, что меньше всего поражению грибков подвержены вещества, состоящие из льняных волокон, а также сульфитная и сульфатная целлюлоза. Искусственные волокна более прочные, чем натуральные. Очевидно, что проблема консервации уже напечатанных на бумаге материалов с каждым годом обостряется. Сейчас странно, когда мы не можем читать старые книги, которые не были сохранены в новых цифровых форматах. Именно поэтому сохранение в достойном состоянии старой бумажной литературы так важно для нас и для будущих поколений, так же актуальна проблема получения так называемого «биоцидного» материала. Имеется в виду такой материал, который может уничтожать бактерии, плесневые грибы и насекомых. В работе использованы глины Горбского месторождения Закарпатской области, которые классифицируются как бентонитовые и имеют требуемую консистенцию с размером частиц от 0,3 до 0,25 мм.

Авторы исследовали сорбцию латексов базальтовыми волокнами. Были исследованы следующие латексы: дивинил метил метакрилат (DMMA), дивинил нитрил (SKN), *изопрен нитрил* (*L-7*). *Был использован метод перезарядки поверхности волокон целлюлозы для получения гибкого и прочного фильтрующего материала. Авторы изучили устойчивость материалов к плесени.*

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

ФУНГІЦИДНО СТІЙКИЙ МАТЕРІАЛ НА ОСНОВІ БАЗАЛЬТОВОГО ВОЛОКНА

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Провідні індустріальні країни демонструють зростання розвитку паперової промисловості навіть більше, ніж інших галузей. Папір був і є дуже важливим для нашої цивілізації. У електротехнічній, радіотехнічній промисловості широко використовуються різні види паперу для виробництва кабелю, конденсаторів, радіодіффузорів, резисторів, телевізорів тощо. У хімічній промисловості папір використовується для хроматографії, електрофорезу і т. д. Але крім очевидних переваг для простого використання, існує необхідність розробки і використання матеріалів, стійких до цвілевих грибів і мікроорганізмів.

Відомо, що найменше схильні вражатися грибами речовини, що складаються з лляних волокон, а також сульфітна і сульфатна целюлоза. Штучні волокна міцніші, ніж натуральні. Очевидно, що проблема зберігання вже надрукованих на папері матеріалів з кожним роком загострюється. Зараз дивно, коли ми не можемо читати старі книги, які не були збережені в нових цифрових форматах. Саме тому збереження в гідному стані старої паперової літератури так важливо для нас і для майбутніх поколінь, так само актуальна проблема отримання так званого «біоцидного» матеріалу. Мається на увазі такий матеріал, який може знищувати бактерії, цвілеві гриби і комах. В роботі використані глини Горбского родовища Закарпатської області, що класифікуються як бентонітові і мають необхідну консистенцію з розміром частинок від 0,3 до 0,25 мм.

Автори досліджували сорбцію латексів базальтовими волокнами. Були досліджені наступні латекси: дивініл метіл метакрілат (DMMA) , дивініл нітрил (SKN), ізопрен нітрил (L-7). Був використаний метод перезарядки поверхні волокон целюлози для отримання гнучкого і міцного фільтруючого матеріалу, а також перевірили стійкість матеріалів до цвілі.

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