Osaulenko K., Demchenko V., Merezhko N.

INVESTIGATION OF THE EFFICIENCY AND POTENTIAL POSSIBILITIES OF PAPER PROTECTION BY SILOXAN IN WET ENVIRONMENTS

Дана оцінка ефективності застосування кремнійорганічних покриттів різного складу для захисту паперу на основі небіленої целюлози у вологих середовищах різного ступеня агресивності. Визначено потенційні можливості їх застосування. Достовірність отриманих даних підтверджена результатами випробувань покриттів на основі метилсиліконату калію і поліетилгідридсилоксанами на поверхні алюмосилікатного скла в гідротермальних умовах і встановлені межі їх ефективного застосування.

Ключові слова: зміцнення паперу, метилсиліконат калію, ступінь екранування, крайовий кут змочування, коефіцієнт ефективності захисної дії.

1. Introduction

Cellulose-based materials are widely used in various industries due to the presence of a complex of valuable physical and chemical properties. Their main advantage is environmental safety. At the same time, the peculiarities of their composition and structure (the presence of hydroxyl groups, high porosity, etc.) necessitate their protection, especially in humid environments. One of the effective ways to solve this problem can be the use of thin-layer silicone coatings. In this regard, the development of such coatings and assessment of their potential application possibilities is topical.

2. The object of research and its technological audit

The object of research is a winding paper based on unbleached cellulose (100 % by weight) thickness 70 ± 3 µm (GOST 1931-80), which has the following properties:

- porosity 55.0 %;
- density (g/cm^3) geometric 0.64 and true 1.42;
- water absorption 58.7 wt. %;
- moisture absorption 17.7 wt. %.

Unbleached pulp-based winding paper is in high demand in the industry as a packaging material. However, one of the most problematic places is that this paper is very unstable when exposed to corrosive media. Therefore, the task is improvement of its properties by siloxane treatment.

3. The aim and objectives of research

The aim of research is evaluation of the effectiveness of the application and the potential for thin-layer silicone coatings of various reactivity for protection of unbleached pulp paper in humid environments.

To achieve this aim, it is necessary to solve the following tasks:

1. To investigate the hydrophobic properties and the fungi resistance of the surface of the treated paper.

2. To carry out a study of the tensile strength and dielectric parameters of the treated paper.

3. To conduct IR spectrometry of porous aluminosilicate glass.

4. Research of existing solutions of the problem

Materials based on plant polymers, in particular cellulose, have a set of valuable physical and technical properties that open up broad prospects for their functional application and for packaging and the production of structural elements [1, 2]. Their special advantage lies in high ecological safety.

Ensuring the availability of a line of necessary qualities is achieved to a large extent due to the use of different types of cellulose and effective methods of its processing into special purpose paper. Particular attention is paid to their effective strengthening by treatment with various chemical preparations (paraffin, polyamide resins, silicates, etc.) [3].

The need to strengthen the paper is due to the high chemical activity of cellulose due to the presence in its composition of a significant number of hydroxyl groups, porosity (up to 60 %) and multi-cycle mechanical loads during operation [4].

Particular attention is required to protect it when operating in wet conditions. The presence of a layer of adsorbed water on the surface can adversely affect the physical and technical properties. The degree of such influence is determined by the energy state of the substrate surface and by the wettability of its water in the liquidcrystal state and the adsorption of water vapor [5, 6].

The effect of sorbed moisture on organic materials can be manifested in the Rehbinder effect, changes in intermolecular interaction, hydrolysis and mechanical destruction [7]. The increase in moisture permeability is promoted by:

 high polarity, especially of the side groups of macromolecules and the presence of numerous double bonds;

- weak ordering of the structure of chemical polymers, greater branching of the side groups and had the symmetry of macromolecules; incomplete measure of the pouring of polymers having reaction groups, etc. [8].

Daily fluctuations in air humidity can accompany sorption and desorption of moisture with cellulose-containing materials. In this case, due to the specific nature of their structure and, as a consequence, the low diffusion coefficient of moisture in some cases, the occurrence of deformations leading to destruction [9] is not ruled out.

Among effective directions in the field of protecting paper and products based on it in humid environments, the use of thin-layer coatings based on organosilicon compounds of different classes deserves attention. Successful use of them requires taking into account the features of its porous capillary structure, small thickness and anisotropy of most physical and technical properties for sheet materials. In addition, no less important are such physicochemical features of cellulose-containing substrates:

- high content of hydroxyl groups in their composition;
- increased hygroscopicity;
- possibility of occurrence of mechanical deformations;
- relatively low mechanical strength in thin layers;

- insignificant chemical resistance to chemical compounds with pH different from neutral;

- a wide range of applications for various functional purposes [10, 11].

5. Methods of research

Modification of the paper surface is carried out by immersion in 3-5 % by volume solutions in water, organic solvents or an aqueous dispersion of organosilicon products:

- potassium methyl siliconate (MSP);

polymethyl-(PMGS) and polyethylhydride siloxane (PEGS);

polymethyl- (PMS) and polyethyl siloxane (PES);
 ethylsilicate hydrolyzate (ESHL) and their modifications based on MSP (MSPM and MSPC) and polyalkylhydride siloxane (PMGSM and PEGSM).

Two-layer coating schemes are applied with an adhesive half-layer based on ethylsilicate hydrolyzate or potassium methyl siliconate and its modifications followed by overlapping of polyalkylhydride siloxane. Curing is carried out by heat treatment at 100–120 °C [12].

The effectiveness of the protective action of silicone coatings is evaluated:

in humid environments (relative humidity 95–98 %, exposure time - 60 days);

- in the presence of microscopic fungi (30 days);

- in the presence of salt fog (25 days, fog water -

2-3 g/m³, dispersity - 1-20 microns) [13].

During the paper test, the following parameters are monitored [14, 15]:

- the contact angle of the surface wetting by water (θ) , degrees;

- change in mass, %;
- fungi resistance, point;
- degree of screening (X), %:
- $X = K(1 \cos \theta_x),$

where $\cos\theta_x$ – the cosine of the surface wetting angle; *K* – tensile strength (as a percentage of the initial).

In addition, it has been proposed to use the comparative efficiency coefficient of the protective action (CECPA), which allows to obtain a more objective picture of the change in the strength of the paper during the testing in comparison with the untreated material [16]:

$$CECPA = (\sigma_c^2 / \sigma_c^1) / (\sigma_u^2 / \sigma_u^1), \qquad (1)$$

where σ_c^2 i σ_c^1 – respectively, the destructive load of coated paper after and before the test; σ_u^2 and σ_u^1 – respectively, the destructive load of uncoated paper after and before the test.

Infrared spectra of siloxanes after curing on the surface of a porous aluminosilicate glass and holding under hydrothermal conditions at a water vapor pressure of 0.8 MPa are recorded on the Specord-75JR (Canada). The choice for the investigation of aluminosilicate glass is due to its chemical inertness and the ability to adsorb a significant number of modifiers, ensuring the necessary reliability of the analysis [17].

The nominal tangent of the dielectric loss angle is measured at a frequency of 1000 Hz after holding the material in a moist medium [18].

6. Research results

Comparison of the obtained data with respect to the wettability of the paper surface after exposure in humid environments of varying degrees of aggressiveness showed an ambiguous change of the latter [19]. The maximum values of the contact angles of wetting at the level of $71-72^{\circ}$, respectively, after 60 days of soaking in a humid environment and 25 days under similar conditions in the presence of salt fog. Their minimum values at 45° are observed after 30 days of exposure in a humid environment with microscopic fungi (Table 1).

Surface treatment with formulations based on industrial organosilicon products, their modifications and two-layer systems allows for a high level of hydrophobicity. The value of the contact angles of water wetting is 96(HEGS)-104(PEGS) degrees after 60 days exposure in moist environment with the use of industrial products and $101-104^{\circ}$ for their modifications and bilayer systems. The degree of screening of the surface is in the range 87.3-92.1 %. The average arithmetic data for the study groups of coatings for edge wetting hangers are at the level of $101.1-103.2^{\circ}$, and the screening degree is 94.2-96.6 %.

The hydrophobic properties of the surface of the treated paper are less stable under conditions of aging for 30 days in a humid environment with microscopic fungi. The marginal angles of wetting with the use of industrial preparations are at the level 69(PES)–83(PEGS) degree, and the screening degree is respectively 50.7–69.4 %.

Modification of siloxanes allows increasing the waterrepellent properties of cellulose-containing substrates to the level of angles θ 78(MSPM)–84(PEGSM) degrees and X - 62.6–70.8 %.

An even better effect is achieved when using two-layer coatings, when the marginal angles increase to a level of 86(MSP/PEGS)-88(ESHL/PMGS, MSPM/PEGS) degrees at a screening degree of 73.5–76.1 %.

According to the arithmetic average, the coverage of fungi in the part of the marginal angles is 77.3, 82.0 and 86.7°, respectively, and shielding is 61.7, 68.0 and 14.4 %, respectively. According to absolute criteria for minimizing the wetting of the paper surface with water, two-layer compositions based on ethylsilicate hydrolyzate and modified methyl siliconate potassium should be noted, followed by overlapping of polyalkylhydride siloxane.

Table 1

	60 days			30 days in the presence of microscopic fungi				25 days in the presence of salt fog		
Type of coating	The contact wetting angle, deg.	Screening degree, %	Weight change, %	Mush- room re- sistance, points	The contact wetting angle, deg.	Screening degree, %	Weight change, %	The contact wetting angle, deg.	Screening degree, %	Weight change, %
Without cover	71	-	11.9	4	45	-	4.4	72	-	1.9
Based on industrial products: MSP	102	95.4	10.1	2	81	66.7	1.8	80	65.2	-4.4
PMGS	103	96.8	8.2	3	82	68.0	2.6	83	69.4	-1.6
PEGS	104	98.1	8.1	2	83	69.4	2.9	84	70.0	-1.9
PMS	102	95.4	7.8	1	77	62.3	2.1	81	66.7	0.4
PES	99	91.4	7.4	0	69	50.7	2.2	83	69.4	0.2
ESHL	96	87.3	8.9	2	75	58.6	2.4	74	58.6	1.5
Based on modified coatings: MSPM	101	94.1	8.7	1	78	62.6	2.3	76	61.2	-5.1
MSPC	102	95.4	8.6	1	79	63.9	2.2	77	62.3	-5.4
PMGSM	104	98.1	6.6	2	83	69.4	2.3	83	69.4	-0.5
PEGSM	102	95.4	6.3	2	84	70.8	2.4	86	73.5	-0.6
two-layer: ESHL/PEGS	103	96.8	7.5	2	87	74.9	2.1	80	70.8	-0.7
ESHL/PMGS	102	95.4	7.3	2	88	76.1	2.0	81	66.7	-0.9
MSP/PEGS	101	94.1	7.6	1	86	73.5	1.8	81	66.7	-4.2
MSPM/PEGS	102	95.4	7.2	1	87	74.9	2.8	82	68.0	-4.5
MSPC/PEGS	104	98.1	7.1	1	88	76.1	2.9	79	63.9	-4.1

Change in properties of paper with silicone coatings after exposure in a humid environment (relative humidity 95–98 %)

Note: the «--» sign means weight reduction.

Among the subjects exposed to wet environments, the exposure for 25 days in the presence of salt mist is accompanied by the most noticeable hydrophilization of the surface of the modified paper. The average arithmetic indices in the corners are $79.7-81.4^{\circ}$, and in the screening degree -65.3-67.7 %.

A more detailed analysis of the dynamics of the change in the last parameter during the tests revealed a similar character for different coatings (Fig. 1). Regardless of the composition of the latter, an increase in the exposure time to 25 days is accompanied by an almost monotonic decrease in the screening degree in the range of 10-20 %. The most noticeable changes occur in the range from 4 to 8 days of testing.

The stay of paper in various moist environments is accompanied by an ambiguous change in its mass (Table 1). From the increase to 11.9 % after 60 days of action of water vapor, to a decrease of 4.4 % after 30 days of simultaneous exposure to moisture and microscopic fungi.

The use of organosilicon coatings significantly reduces moisture absorption to 47 % (PEGSM) in the first case and up to 60 % (MSP, MSP(PEGS)) exposure in a humid environment with microscopic fungi. Fungal resistance of the modified paper grows from 4 to 1-2 points.

The presence of salt fog in a humid environment has an ambiguous effect on the change in the mass of paper with silicone coatings. Against the background of its growth by 1.9 % for the initial material, a decrease due to surface treatment with modified siloxane to 0.5-5.1 % or an increase of 0.1-1.5 with the use of polyalkyl siloxanes and hydrolyzate of ethylsilicate is possible.

Destructive processes that occur in the composition of unbleached pulp paper and are manifested by hydrophilization of its surface (after exposure in humid environments of varying degrees of aggressiveness) and changes in mass are accompanied by deterioration in the mechanical strength of the latter. Its decrease for the starting material is from 21.5 (60 days in a humid environment) to 60 % (after 30 days of exposure to moisture and the presence of microscopic fungi) (Table 2).

The surface treatment of paper by organosilicon compounds of various compositions allows cardinal stabilization of its tensile strength [20]. So, after 60 days of exposure, the change of the latter for the vast majority of coating systems is from 3.8(MSPC) to 0.6(ESHL/PEGS). The minimum values of the comparative efficiency coefficient of the protective action, which makes it possible to evaluate the changes in mechanical strength, taking into account the behavior of the substrate itself during the testing and the degree of protection by the silicone coating, were noted at the level of 1.03 when treated with potassium methyl siliconate. This is due primarily to its low stabilizing ability in terms of tensile strength (89.3 % versus 78.4 % in paper without finishing).

According to the absolute level of the evaluated indicators, the advantage in this type of testing belongs to poly (methylhydric) siloxane in combination with ethylsilicate hydrolyzate (tensile strength is 99.4 % of the initial value).

In wet environments with microscopic fungi, the basic silicone compounds provide a mechanical stability of 86.1(MSP)-93.2(ESHL) % of the initial strength. The effectiveness of the protective action is estimated by a factor of 1.03(PMS)-1.09(PMGS).

Modified organosilicon compounds provide mechanical strength in the range of 93.1(MSPC)–97.1(PEGSM) % of the initial at CECPA levels of 1.02(PMGSM)–1.18(MSPC).



Fig. 1. Change in the screening degree of paper with an organosilicon coating when exposed in a humid environment in the presence of salt fog: a - ESHL/PEGS and MSPM/PEGS; b - PESGM and MSPC; c - PEGS and MSP

Table 2

Type of coating	60	days	30 days in the presence of microscopic fungi		25 days in the presence of salt fog				
	Tensile force	CECPA	Tensile force	CECPA	Tensile force	CECPA			
Without cover	78.4	-	39.7	-	64.2	-			
Based on industrial products: MSP	89.3	1.03	86.1	1.04	85.5	1.15			
PMGS	96.7	1.22	89.1	1.09	90.3	1.14			
PEGS	97.2	1.27	88.6	1.08	89.2	1.15			
PMS	98.4	1.07	89.7	1.01	91.2	1.03			
PES	99.0	1.07	88.4	1.06	90.4	1.02			
ESHL	97.8	1.17	93.2	1.07	93.6	1.07			
Based on modified coatings: MSPM	96.2	1.15	93.1	1.05	88.5	1.00			
MSPC	97.1	1.14	96.3	1.18	84.6	0.96			
PMGSM	98.4	1.11	95.7	1.02	92.1	1.01			
PEGSM	98.7	1.12	97.1	1.05	92.6	1.02			
Two-layer: ESHL/PEGS	99.4	1.11	97.2	1.03	94.4	1.02			
ESHL/PMGS	99.2	1.13	96.6	1.04	93.7	1.01			
MSP/PEGS	95.6	1.10	94.5	1.05	84.7	0.94			
MSPM/PEGS	98.1	1.09	95.2	1.11	103.3	0.99			
MSPC/PEGS	98.4	1.06	95.3	1.09	85.4	0.98			

Tensile strength (% of paper with silicone coatings (% to original) after exposure						
in moist environment (relative humidity 95–98 %))						

ВИРОБНИЧО-ТЕХНОЛОГІЧНІ СИСТЕМИ:

Two-layer coatings, which in the previous version of testing are more effectively provide stability of paper strength in a moist environment in the presence of microscopic fungi. The maximum (97.7 % of the strength from the initial) and the minimum (91.8 %) effects are achieved by using modified methyl siliconate potassium in combination with polyethylhydride siloxane. The level of the protective action coefficient is from 1.03(ESHL/PEGS) to 1.11(PMGSM/PEGS).

The best effect on the preservation of the tensile strength of paper among the studied compositions according to CECPA is recorded with the application of MSPC/PEGS.

The tensile strength of paper after exposure to salt mist in combination with a moist medium occupies an intermediate position among the test variants described above [21]. The tensile force is reduced to 64.2 % of the initial force.

It is established that the effectiveness of the protective action of silicone coatings in terms of preserving the strength of paper is determined, first of all, by the composition of the latter. Regardless of the schemes of their application, a less tensile force at the level of 84.6–90.1 % of the initial value is fixed when using coatings based on potassium methylsiliconate and its derivatives in various combinations. The exception is the MSPC/PEGS system (tensile force of 103.3 %). Other coatings in this test variant provide a level of retention of the tensile strength of 89.2(PEGS)– 94.4(ESHL/PEGS) % of the starting and CECPA in the interval 1.01(PMGSM, ESHL/PMGS)–1.15(PEGS).

A comparative analysis of the obtained results with respect to the mechanical strength of paper in a moist medium in the presence of salt fog shows an advantage of iodized and two-layer coatings based on polyalkylhydride siloxane (tensile force remains at the level of 92.1-94.4 %).

The reliability degree of the obtained results, as well as an assessment of the potential capabilities of the main types of siloxanes for protection against moisture, is carried out by keeping the latter on the surface of a porous aluminosilicate glass under hydrothermal conditions (water vapor pressure up to 0.8 MPa, exposure time up to 8 hours) [21, 22]. The choice of such substrate is due to the fact that, in contrast to porous paper, it allows a greater number of modifiers to be adsorbed in a dispersed state. In addition, such a support can have a similar mechanism of interaction with potassium methylsiliconate and polyethylhydride siloxane with hydroxyl groups on its surface. All this allows to objectively assess the stability of siloxanes specifically for the destructive effect of moisture, despite the chemical composition of the substrate [23].

The obtained results using independent methods of physicochemical analysis (determination of the conditional dielectric loss tangent and IR spectral analysis) confirmed the independent advantage of using polyalkylhydride siloxanes for paper protection in moist environments (Fig. 2, 3). Thus, according to measurements of dielectric parameters, it can be asserted that the protective effect of potassium methylsiliconate effectively only works on the pressure of water vapor at a level of 0.6 MPa. While the use of polyethylhydride siloxane is possible over a wider range: in addition, the value of the tangent of the dielectric loss angle when applied is almost an order of magnitude lower than that of potassium methylsiliconate.

The high chemical stability of polyethylhydride siloxane under hydrothermal conditions is also confirmed by IR spectral analysis.

Taking into account the features of the infrared spectra of the aluminosilicate matrix, the characteristics of the absorption band in the frequency interval are chosen for comparison:

- 1460-1480 cm⁻¹ (vibrations of the -Si-R groups) for methyl potassium siliconate;
- at 855 cm⁻¹ (-Si-H) and 800-820 cm⁻¹ (-Si-OH) for potassium polyethyl siliconate.

It is established that in the first case the absorption intensity for the characteristic bands decreases somewhat (up to 5–7 %), which indicates a decrease in the methyl radicals and agrees well with the data obtained in the determination of tg δ . A more complex picture is observed for polyethylhydride siloxane. It is due to the course of its interaction with the glass surface with the participation of –Si–H bonds and hydration of the latter with the appearance of free hydroxyl groups under the action of superheated water vapor. However, despite the complexity of the described processes, the energy state of the surface of the modified glass remains practically unchanged.



Fig. 2. The influence of hydrothermal treatment on the dielectric properties of cellular aluminosilicate glass impregnated with siloxane



Fig. 3. IR spectra of porous aluminosilicate glass impregnated with siloxanes after hydrothermal treatment (pressure: 0.8 MPa, 8 hours): a - potassium methylsilicilate; b - polyethylhydride siloxane

7. SWOT analysis of research results

Strengths. Among the strengths of this research, it should be noted that the use of thin-layer coatings based on organosilicon compounds of different classes deserves attention among the effective directions of paper protection in humid environments. Successful use of the latter requires taking into account the features of the porous capillary structure, the small thickness and anisotropy of most physical and technical properties of the paper.

A study of the efficiency and potential of siloxane paper protection in humid environments will expand the scope of use of this material. In addition, the treatment of the surface of the paper with formulations based on industrial silicone products, their modifications and two-layer systems allows to ensure a high level of its hydrophobicity.

Processing of the paper surface with organosilicon compounds of various compositions allows cardinally stabilizing its tensile strength.

Weaknesses. The weak side of these researches is that they are insufficient for a complete and comprehensive evaluation of organosilicon thin-film coatings to determine all the properties of the latter. The presence of a layer of adsorbed water on the surface of organosilicon thin-film coatings can adversely affect the physical and technical properties. The degree of such influence is determined by the energy state of the surface of the substrate and by the wettability of its water in the liquid-crystal state and the adsorption of water vapor.

Another weak side of this research is that the above studies are conducted over a long period of operation in real time. As a result, there may be errors due to subjectivity of research. Therefore, in order to prevent this shortcoming, it is necessary to pay special attention to the purity of the scientific experiment at all its stages. To prevent shortcomings and inaccuracies in the course of research, it is necessary to follow the methods of research and purity of the experiment.

Opportunities. In the long term, it is advisable to carry out other studies related to the determination of physicalchemical, physical-technical and physical-mechanical properties of organosilicon thin-layer coatings. Investigation of these properties of organosilicon thin-layer coatings will allow to determine more deeply the expediency of using different compositions of the latter for paper protection in humid environments. Research in this direction can expand the scope of application of organosilicon thin-layer coatings, as well as obtain the maximum economic effect with minimal financial investment.

Threats. Difficulties in implementing the results obtained may be due to the fact that this material is not as wellknown as, for example, polymer coatings. The properties of the latter have been widely studied by various scientists. However, despite this, the obtained results of investigation of the effectiveness and potential possibilities of siloxane paper protection in damp environments give rather wide opportunities and prospects for using the latter in the construction industry.

Thus, SWOT analysis of research results allows to determine the main directions for achieving the research objective, namely:

 to conduct comprehensive studies to determine the effectiveness and potential of siloxane paper protection in humid environments; to develop a methodology for additional studies of the properties of organosilicon thin-layer coatings;

- to investigate the individual characteristics of the modified organosilicon thin-film coatings with a view to further recommending their use in the construction industry.

8. Conclusions

1. The hydrophobic properties and the fungi resistance of the surface of the treated paper are investigated and the advantage of modified and two-layer siloxane coatings, the parameters of which are equal:

- the contact angle of the surface wetting by water $(\theta = 101 - 104^{\circ});$

- fungi resistance (1–2 points).

2. A study of the tensile strength of treated paper is made and its level of 84.6-103.3 % against 39.7-78.4 % in unprotected paper with stable values of the dielectric parameters is fixed.

3. Based on the IR spectrometry of porous aluminosilicate glass impregnated with siloxane, as stable under hydrothermal conditions, substrate, the prospects of using the latter for protection are shown. This is because the decrease in the intensity of the characteristic bands does not exceed 5-7 %.

References

- Pulp and Paper Online. URL: https://www.pulpandpaperonline. com/ (Last accessed: 11.12.2017).
- Yan L.-Y., Li S.-Y., Song X.-L. Preparation of Paper Strengthening Agent by Esterification of Cellulosic Fines // BioResources. 2016. Vol. 12, No. 1. P. 469–477. doi:10.15376/biores.12.1.469-477
- 3. Ashori A., Nourbakhsh A. A comparative study on mechanical properties and water absorption behavior of fiber-reinforced polypropylene composites prepared by OCC fiber and aspen fiber // Polymer Composites. 2008. Vol. 29, No. 5. P. 574–578. doi:10.1002/pc.20582
- 4. Landel R. F., Nielsen L. E. Mechanical Properties of Polymers and Composites. CRC Press, 1993. 580 p.
- Modification of properties of old newspaper pulp with biological method / Chen Y. et al. // Bioresource Technology. 2010. Vol. 101, No. 18. P. 7041–7045. doi:10.1016/j.biortech. 2010.04.015
- Dienes D., Egyhazi A., Reczey K. Treatment of recycled fiber with Trichoderma cellulases // Industrial Crops and Products. 2004. Vol. 20, No. 1. P. 11–21. doi:10.1016/j.indcrop.2003.12.009
- Marton J., Roberts J. Dry-strength additives // Paper Chemistry. New York: Springer, 1996. P. 83–97. doi:10.1007/978-94-011-0605-4_6
- Wang J., Zhang J. Application status and research developments of paper dry strength // Thermosetting Resin. North Carolina, 2014. P. 53–58.
- Yang D., Li H., Li X. Study on the cationic emulsifuing dry strength agents of paper. Vol. 1. Shandong: Shandong Chemical Industry, 2004. P. 3–5.
- Astratov M. S., Homelia M. D., Movchaniuk O. M. Tekhnolohiia pererobky paperu i kartonu. Part 1. Kyiv: NTUU «KPI», 2007. 231 p.
- Koptiukh L. A. Novi tekhnolohii i protsesy stvorennia pakuvalnoho paperu ta filtruvalnoho kartonu dlia kharchovoi promyslovosti: Abstract's Thesis of the Doctor of Sciences. Kyiv, 1998. 33 p.
- Karyakina M. I. Ispytanie lakokrasochnykh materialov i pokrytiy. Moscow: Khimiya, 1988. 272 p.
 Prymakov S. P., Barbash V. N. Tekhnolohiia paperu i kartonu.
- Prymakov S. P., Barbash V. N. Tekhnolohiia paperu i kartonu. Kyiv: EKMO, 2002. 396 p.
- Lakokrasochnye materialy i pokrytiya. Teoriya i praktika / ed. by Lamburn R. Saint Petersburg: Khimiya, 1991. 512 p.
- Davis J. R. Surface Engineereing for Corrosion and Wear Resistance. ASM International, 2001. 257 p.

- Parfitt G. D., Sing K. S. W. Characterization of Powder Surfaces. London: Academic Press, 1976. 348 p.
- Applied Infrared Spectroscopy: Fundamentals Techniques and Analytical Problem-Solving / ed. by Smith A. L., Elving P. J., Winefordner J. D., Kolthoff I. M. John Wiley & Sons, Inc., 1979. 336 p.
- Brok T., Groteklaus M., Mishke P. Evropeyskoe rukovodstvo po lakokrasochnym materialam i pokrytiyam / ed. by Tsorll U. Moscow: Peynt-Media, 2004. 548 p.
- **19.** Mostyka K. V. Formuvannia vlastyvostei vodonepronyknykh paperovykh pakuvalnykh materialiv dlia kondyterskykh vyrobiv: Abstract's PhD thesis. Kyiv, 2012. 21 p.
- 20. Sviderskyi V. A., Salnyk V. H., Cherniak L. P. Fizyko-khimichni vlastyvosti poverkhni kaoliniv i kaoliniievmisnykh hlyn ta yikh vydnykh dyspersii. Kyiv: Znannia, 2012. 166 p.
- Karyakina M. I. Ispytanie lakokrasochnykh materialov i pokrytiy. Moscow: Khimiya, 1988. 272 p.
- Pashhenko A. A., Sviderskiy V. A. Kremniyorganicheskie pokrytiya dlya zashhity ot biokorozii. Kyiv: Tekhnika, 1988. 136 p.
- 23. Sviderskyi V. A., Cherniak L. P., Salnyk V. H. Instrumentalni metody khimichnoho analizu sylikatnykh system. Kyiv: National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», 2017. 171 p.

ИССЛЕДОВАНИЕ ЭФФЕКТИВНОСТИ И ПОТЕНЦИАЛЬНЫХ возможностей защиты бумаги силоксанами во влажной среде

Дана оценка эффективности применения кремнийорганических покрытий различного состава для защиты бумаги на основе небеленой целлюлозы во влажных средах различной степени агрессивности. Определены потенциальные возможности их применения. Достоверность полученных данных подтверждена результатами испытаний покрытий на основе метилсиликоната калия и полиетилгидридсилоксанами на поверхности алюмосиликатного стекла в гидротермальных условиях и установлены границы их эффективного применения.

Ключевые слова: укрепление бумаги, метилсиликонат калия, степень экранирования, краевой угол смачивания, коэффициент эффективности защитного действия.

Osaulenko Kseniia, Postgraduate Student, Department of Commodity and Customs Affairs, Kyiv National University of Trade and Economics, Ukraine, e-mail: Sky.07@meta.ua, ORCID: https:// orcid.org/0000-0002-0522-3006

Demchenko Valentyna, Postgraduate Student, Department of Commodity and Customs Affairs, Kyiv National University of Trade and Economics, Ukraine, e-mail: tina76748@gmail.com, ORCID: https://orcid.org/0000-0001-7527-2236

.....

Merezhko Nina, Doctor of Technical Sciences, Professor, Head of the Department of Commodity and Customs Affairs, Kyiv National University of Trade and Economics, Ukraine, e-mail: neprod2@knteu.kiev.ua, ORCID: https://orcid.org/0000-0003-3077-9636

UDC 691.32:629.5 DOI: 10.15587/2312-8372.2018.124176

Kyrychenko K., Shchedrolosiev O., Rashkovskyi O.

USE OF HIGH-PERFORMANCE PLASTICIZERS TO PROVIDE DESIGN AND OPERATIONAL REQUIREMENTS FOR THE CONCRETE COMPOSITION FOR THE CONSTRUCTION OF FLOATING COMPOSITE DOCKS

Розглянуті особливі вимоги, які пред'являються до суднобудівного бетону і бетонної суміші у зв'язку із екстремальними умовами роботи морських залізобетонних споруд. Наведена класифікація пластифікуючих добавок за ефективністю пластифікуючої дії. Розглянуто допустимий вміст шкідливих домішок у заповнювачах для важких бетонів. Наведені умови забезпечення тріщиностійкості бетону. Проведені дослідження дозволяють визначити рекомендований гранулометричний склад піску і щебеню, які використовуються для суднобудівного бетону.

Ключові слова: плавучий композитний док, суднобудівний бетон, пластифікуючі добавки, суперпластифікатори, міцність бетону.

1. Introduction

The working conditions of marine reinforced concrete structures (especially floating docks) are largely extreme. Reinforced concrete structures of floating docks are exposed to all known environmental influences due to the fact that they are operated in all climatic zones of the globe. At the same time, the structures of the floating dock experience the following loads: permanent (cargo on the deck, water pressure, etc.);
static variables (forces of water ejection during deflection and bending of the shell);

- dynamic variables (impacts, invasions), as a result of which stresses of different magnitude and variable direction arise in the concrete.

The advantage of reinforced concrete is that concrete itself works well for compression, and tensile work is provided by reinforcing steel, which is protected from aggressive

19 —