УДОСКОНАЛЕННЯ ВЛАСТИВОСТЕЙ ТОВАРІВ

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WATERPROOF PAPER PACKAGING MATERIALS: EVALUATION OF PROPERTIES

The results of studies of the properties of paper obtained by surface treatment of a composition based on polyamide-amine-epichlorohydrin, polyvinyl alcohol and urea are presented. A comparative assessment of the quality of industrial moisture-proof waterproof paper packaging materials and foreign-made parchment as the closest analogue was carried out.

Keywords: paper packaging materials, hydrophobic composition, polyvinyl alcohol, polyamidamine pichlorhydrin, urea.

Осыка В., Комаха В., Комаха О. Влагопрочные бумажные упаковочные материалы: оценка свойств. *Приведены результаты исследований свойств бумаги, полученной поверхностной обработкой композиции на основе полиамидаминепихлоргидрина, поливинилового спирта и карбамида. Проведена сравнительная оценка качества изготовленных в промышленных условиях влагопрочных водонепроницаемых бумажных упаковочных материалов и подпергамента иностранного производства как ближайшего аналога.*

Ключевые слова: бумажные упаковочные материалы, гидрофобный состав, поливиниловый спирт, полиамидаминепихлоргидрин, карбамид.

Background. Improving barrier and protective properties, resistance to moisture (water, steam) and air are the main requirements for wrapping paper [1–3]. Such materials must also maintain high mechanical strength in dry and wet conditions to ensure the reliability of packaging and protection packaged products from the environment [4].

Results of studies [5–6] show that the mechanical strength of dry paper can be adjusted by changing the degree of grinding cellulose fibers. This is explained by the increase in the intensity of the weave of the fibrillated fibers [7–8], however, this method does not provide the strength of the paper in the wet state.

The works of J. Toland [9], P. Samyn [10], C. Silvestre [11] are devoted to the problems of paper-based packaging materials and the study of their properties. In particular, these authors propose to use polymer coatings to obtain packaging materials with the desired properties.

In researches of scientists which are devoted to problems of manufacturing of paper packing materials with the set properties attention is paid only to separate parameters.The general set of properties of paper packaging materials, which are able to provide polymer coatings, is insufficiently studied.

Analysis of recent research and publications. Previous studies have shown that the most effective fibrous raw material for the production of paper-base for moisture-resistant waterproof packaging materials is sulfate unbleached cellulose of coniferous and hardwoods with the optimal degree of grinding of cellulose fibers 55–65 °SR [12]. Also, previously scientifically substantiated and proved the effectiveness of epichlorohydrin resins in a composition with polyvinyl alcohol [13] to give paper packaging materials barrier and protective properties, developed mathematical models and obtained the composition of a hydrophobic composition for processing paper-base that provides optimal properties [14].

The aim of the study is to investigate the properties of paper packaging materials developed with using a hydrophobic composition and compare them with the nearest analogue.

Materials and methods. *The object of the study is* paper packaging materials made by treating the base paper with a hydrophobic composition.

Sulphate unbleached pulp of coniferous wood of the NS-2 brand of production of JSC Baltic Cellulose (RF) and hardwood of the NS-3 brand of wood of JSC Svetlogorsk Pulp and Cardboard Plant (Belarus) were used. Paper samples were made from a composition of these coniferous and deciduous pulp at a ratio of 80:20, ground to a degree of grinding of 65 °C.

Fibrous semi-finished products were subjected to dissolution and grinding in the presence of water in the laboratory role of *VALLEY* at a drum speed of 500 rpm. The degree of grinding was monitored on a Schopper-Riegler device according to standard methods. The test paper samples were prepared using a sheet-fed laboratory instrument with a combined *Rapid Kothen* drying chamber.

To give the paper packaging materials moisture resistance and water resistance, the base paper was subjected to surface treatment with compositions using aqueous solutions of polyamidoamine epichlorohydrin (PAAEH), polyvinyl alcohol (PVA) and urea.

To give the paper packaging materials moisture resistance and water resistance, the base paper was subjected to surface treatment with compositions using aqueous solutions of PAAEH, polyvinyl alcohol and urea.

The preparation of the composition was performed by preparing aqueous solutions of the components and mixing them ($\tau \approx 20–30$ min., T = 30–35 °C). The composition [14] was applied to the surface of the base paper, the paper was dried, kept for 10 days and subjected to tests according to methods and regulations adopted in the pulp and paper industry [15–20].

Studies of the microstructure of the paper surface were performed by electron microscopy on a scanning electron microscope *Jeol JSM-6700F* with energy dispersion system for microanalysis *JED-2300* (accelerating voltage $15 \cdot 10^3$ V).

Results.The set of barrier properties of the developed moisture-resistant waterproof paper packaging materials was evaluated by the indicators of surface absorbency, air permeability and water permeability. Paper of different weight (45–60 g/m^2) and density (0.65–0.75 g/cm^3) was used as a basis for packaging materials. This led to significant differences in the values of the indicators that characterize the barrier properties of the developed types of packaging paper *(Table 1).*

Table 1

Barrier properties of developed moisture-resistant waterproof paper packaging materials and the nearest analogue

Characteristic	Moisture-resistant waterproof paper packaging materials			Parchment
	B-50	B-55	B-65	
Mass of material with an area of 1 m^2, g	49.2	56.3	66.4	55.3
Density, g/cm^3	0.68	0.72	0.79	0.78
Humidity, %	7.2	7.3	7.0	7.2
Air permeability, cm^3/min	24	16	12	40
Surface absorbency, g/m^2	24.1	20.2	18.5	45.2
Water permeability, s	2250	2470	2840	2100

The quality of the developed moisture-resistant waterproof paper packaging materials was compared with the closest analogue. For packaging paper brand B-55 as an analogue selected parchment made in Finland, made by gluing, which in its quality corresponds to the parchment according to GOST 1760–2014.

Compared to parchment, the developed materials have better barrier properties. In particular, B-55 paper has 2.5 times less air permeability, 2.2 times less surface absorbency and 15 % less water permeability, although the weight of 1 m^2 of these materials corresponds to the level of 55 ± 2 g/m^2.

The developed materials differ in the weight of 1 m^2 and the density of the base paper used for their production. Accordingly, such materials differ in the level of initial indicators, which as a consequence affects the properties of the manufactured packaging materials. The highest indicators of resistance to water (2840 s) and air (12 cm^3/min), and the lowest surface absorbency (18.5 g/m^2) has a sample with a higher density and mass per unit area.

Packaging paper (B-50) with the lowest weight (49.2 g/m^2) and density (0.68 g/cm^3), among the developed, has a slightly higher water permeability (2250 s) and surface water absorption (24.1 g/m^2). The amount of air passing through such paper has doubled, compared to the paper B-65 – 24 against 12 cm^3/min.

The developed coating provides the paper with increased impermeability to water and air and limits the permeability to light rays, which contributes to the comprehensive protection of products and extends its shelf life. The results of tests of samples of wrapping paper and parchment for light transmission are shown in *Figure 1.*

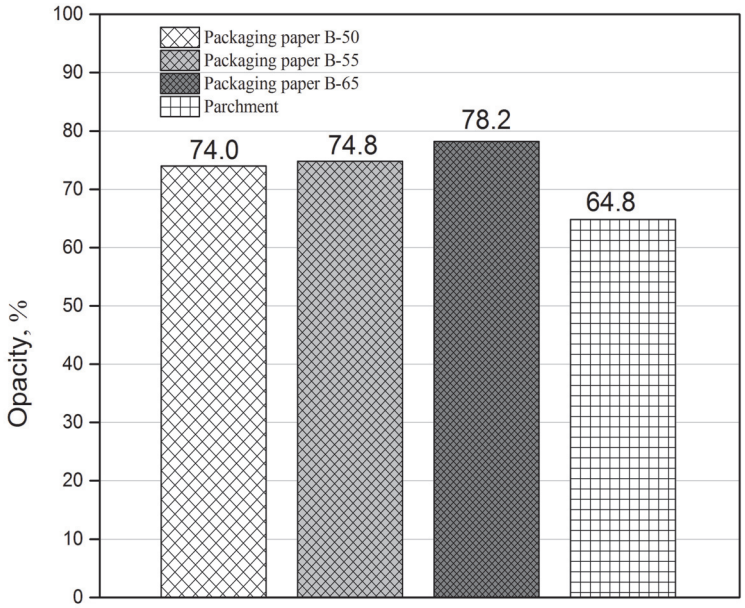
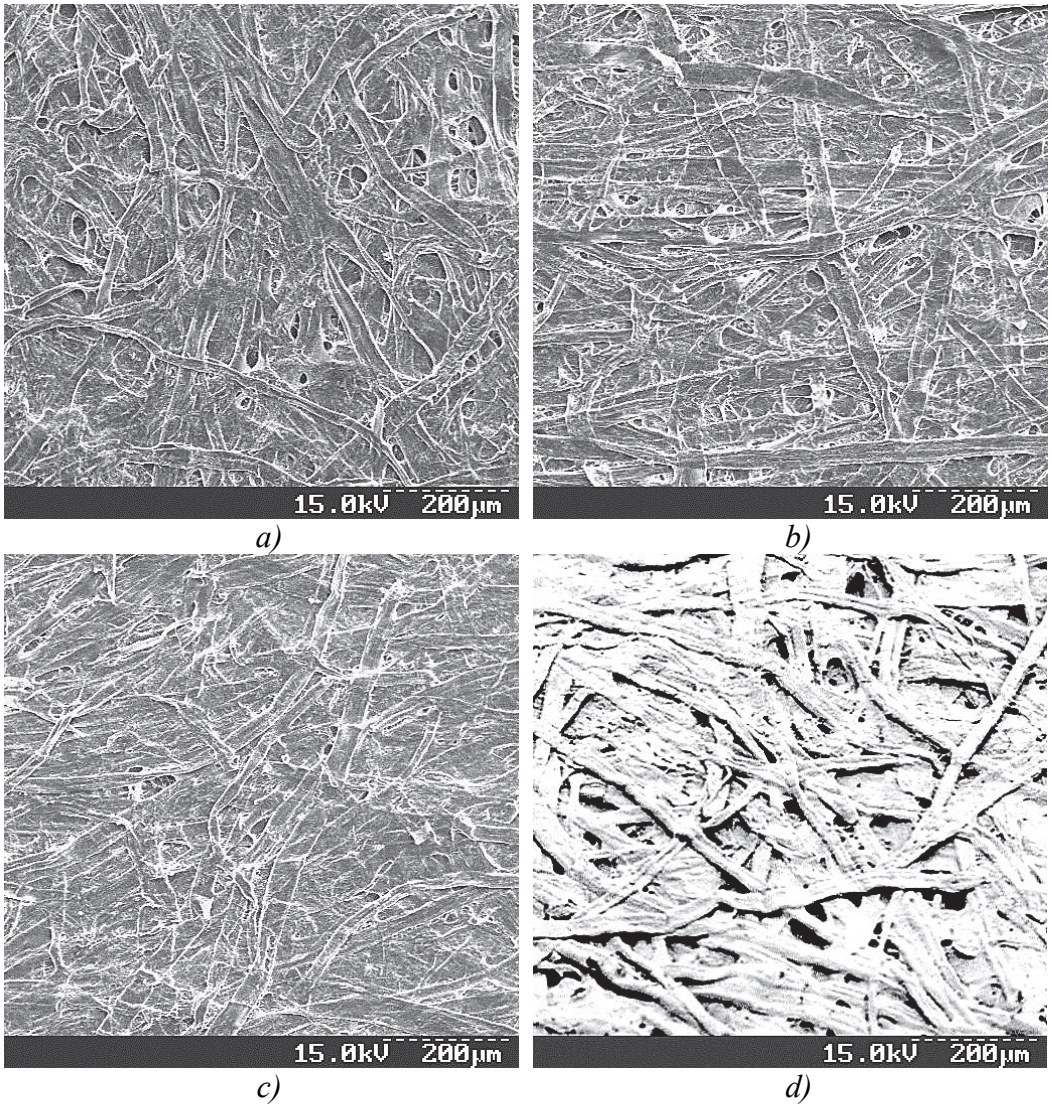


Figure 1. Impermeability of samples of paper packaging materials

In this case, the opacity of the paper was ensured by the use in the composition of the base paper of more dispersed cellulose of coniferous wood ground to a degree of 65 °C, compaction of the structure of the paper web and its surface treatment. The opacity of the developed packaging materials is at the level of 74–78.2 % depending on the density and weight of 1 m^2 of paper and exceeds the level of parchment by an average of 10 %.

An important indicator of paper packaging materials is the morphology and structure of the cellulose fibers from which they are made. Electron-microscopic images of the studied samples of the developed packaging materials and parchment *(Figure 2)* give an idea of the nature of the distribution of cellulose fibers in the material, allow to estimate their transverse dimensions, visually examine the macrostructure of the surface.



a) *b)* *c)* *d)*

Figure 2. Electron microscopic images (200 times magnification) of the surface of moisture-resistant waterproof packaging materials: *a)* B-50; *b)* B-55; *c)* B-6; *d)* parchment

Cellulose fibers in samples of packaging paper obtained by treatment with a hydrophobic composition are characterized by a greater degree of fibrillation. The formation of interfiber bonds is better observed in the images of the developed material (See *Figure 2*, *a–c*) than in the image of the parchment (See *Figure 2, d*).

The waterproofness of the packaging material depends on the structural density of the base paper and the condition of its surface, the presence of surface treatment with substances that can repel water.

The results of research and testing of packaging materials indicate a high level of destructive force of the developed packaging paper in the machine and transverse directions, which is evidence of the uniformity of the mechanical strength of the material *(Table 2).*

Table 2

Mechanical properties of the developed moisture-resistant waterproof paper packaging materials and the nearest analogue

Characteristic	Moisture-resistant waterproof paper packaging materials			Parchment
	B-50	B-55	B-65	
Mass of material with an area of 1 m^2, g	48.2	56.3	66.4	55.3
Destructive force, N:				
- in the machine direction:				
in the dry state	60.4	72.0	76.5	48.0
in a wet state	21.2	26.4	29.6	8.5
- in the transverse direction:				
• in the dry state	54.2	60.0	64.1	35.0
• in a wet state	16.4	20.3	22.5	6.8
Moisture resistance, %				
- in the machine direction	35.0	36.7	38.7	18.0
- in the transverse direction	30.2	34.0	35.1	20.0
Relative elongation at the time of failure, %:				
- in the machine direction	3.3	3.3	3.5	2.6
- in the transverse direction	7.6	7.4	7.2	3.8
Fracture toughness during repeated bends.:				
- in the machine direction	655	673	697	325
- in the transverse direction	746	772	784	384
Resistance to pushing, kPa	366	428	446	284

It should be noted that the parchment also has a fairly high level of mechanical properties in the dry state, which exceeds the standards provided, but in terms of destructive force in the wet state is significantly inferior to the developed materials.

To assess the mechanical properties of packaging materials, their humidity is one of the most important factors. Therefore, the destructive force in the machine and transverse directions was measured in dry and wet conditions.

The destructive force of the developed paper in the machine direction in the dry state (humidity 7–9 %) is more in 2.5–3.5 times and in the transversedirection – 1.54–1.83 times higher than in the parchment, depending on the density and weight of 1 m^2 of material. The strength of the paper in the transverse direction is less than in the machine, which is due to the fact that the cellulose fibers in the process of pouring the paper are oriented mainly in the machine direction.

The developed packaging materials have higher, compared to parchment, indicators of destructive force in the wet state. In the machine direction, this figure is 2.5–3.5 times higher, in the transverse – 2.4–3.1 times. Parchment has a much lower moisture resistance in both machine and transverse directions – 18 and 20 %, concordantly.

High wet strength of the developed packaging materials is achieved through a comprehensive approach to the formation of the strength of the base paper by developing a fibrous composition based on hardwood and

softwood pulp with different fiber lengths, degree of grinding, density and weight of paper fabric made from them, and the appropriate level of properties of the base paper and ensuring their preservation and preservation in the wet state after surface treatment with a hydrophobic composition based on PAAEH.

Relative elongation is an important indicator of packaging paper for automated packaging (wrapping) of products, during which paper with a low relative elongation is torn, thereby violating the integrity of the package. The value of this indicator in the transverse direction is especially important, because the destructive force in this case is much less than in the machine.

The elongation at the moment of fracture in the transverse direction for the developed paper B-50 is – 7.6 %. With increasing material density, the value of the indicator decreases slightly to the level of 7.4 and 7.2 % for packaging paper brands B-55 and B-65, respectively. The relative elongation in the machine direction is at the level of 3.3–3.5 %. For comparison in the parchment: 2.6 % – in the machine and 3.8 % – in the transverse directions.

The maximum number of double bends that the paper can withstand is characterized by the fracture toughness of the paper and its resistance to dynamic loads. The ability of paper to withstand static loads is characterized by resistance to punching. All other things being equal, these paper figures depend on the strength of the bond between the cellulose fibers and their flexibility. Sample paper B-55 has twice the breaking strength in both directions and 1.5 times greater resistance to puncture compared to parchment of the same mass of 1 m^2, which is achieved by using different lengths of cellulose fibers and the formation of more interfiber bonds due to use of hydrophobic composition.

The results of the research showed the practical possibility of obtaining moisture-resistant waterproof packaging material with the predicted level of properties by adjusting the composition and structure of the base paper and hydrophobic composition for surface treatment, which achieves high barrier, physico-mechanical, protective and operational properties of packaging material. which allow to use it for packing of various types of production of food, pharmaceutical, light and other industries.

Conclusion. The developed moisture-resistant waterproof paper packaging materials have increased water resistance, moisture resistance and other strength and barrier properties, reduced level of surface water absorption compared to the nearest composition and structure, as well as the scope of application of the analogue – subparchment.

Based on complex studies obtained using the hydrophobic composition of moisture-resistant waterproof paper packaging materials, it was found that the indicators of water permeability (2250–2840 s), surface absorbency (18.5–24.1 g/m^2) and mechanical strength in the dry state (60.4–76.5 N) developed PM exceed the parchment (105 s, 45.2 g/m^2 and 48 N, respectively), while ensuring a sufficient level of air exchange of the packaged moisture-containing product with the environment (air permeability is 12–24 cm^3/min), as well as significantly increases the mechanical strength of the material in the wet state 21.2–29.6 N.

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Осика В., Комаха В., Комаха О. Вологоміцні паперові пакувальні матеріали: оцінка властивостей.

Постановка проблеми. Підвищення бар'єрних і захисних властивостей опору проникненню вологи та повітря є основною вимогою, що висувають до пакувального паперу. Такі матеріали мають зберігати високу механічну міцність у сухому та вологому станах для забезпечення надійності паковання, захисту властивостей упакованої продукції від впливу навколишнього середовища.

Мета статті – порівняльне дослідження властивостей паперових пакувальних матеріалів (ППМ), розроблених з використанням гідрофобної композиції? та найближчого аналога – підпергаменту.

Матеріали та методи. Зразки паперу виготовлено з композиції хвойної (марки НС-2 від АТ "Балтійська целюлоза", РФ) та листяної (марки НС-3 від АТ "Світлогорський целюлозно-картонний комбінат", Білорусь) целюлози за співвідношення 80:20, розмеленої до ступеня помелу 65 °ШР.

Волокнисті напівфабрикати піддавали розпуску та розмелюванню в присутності води в лабораторному ролі *VALLEY* за швидкості барабана 500 об/хв. Ступінь

помелу контролювали на приладі Шоппер-Ріглера за стандартною методикою. Досліджувані зразки паперу готували за допомогою листовиливного лабораторного приладу із комбінованою сушильною камерою *Rapid Kothen*.

Паперові пакувальні матеріали отримано поверхневим обробленням композиціями з використанням оптимальних водних розчинів поліамідамінепіхлоргідрину, полівінілового спирту та карбаміду. Приготовані водні розчини змішували ($\tau \approx$ 20–30 хв., T = 30–35 °C) і наносили на поверхню паперу-основи, папір висушували, витримували 10 діб.

Дослідження мікроструктури поверхні паперу проведено методом електронної мікроскопії на растровому електронному мікроскопі *Jeol JSM-6700F* з енергодисперсійною системою для мікроаналізу *JED-2300* (прискорююча напруга $15 \cdot 10^3$ В).

Результати дослідження. Комплекс бар'єрних властивостей розроблених вологоміцних водонепроникних ППМ оцінено за показниками поверхневої вбирності, повітропроникності та водопроникності. Як основу для пакувальних матеріалів використано папір різної маси (45–60 г/м^2) та щільності (0.65–0.75 г/см^3). Якість розроблених вологоміцних водонепроникних паперових пакувальних матеріалів порівнювали з найближчим аналогом – підпергаментом виробництва Фінляндії.

Проти підпергаменту розроблені матеріали мають кращі показники бар'єрних властивостей. Зокрема, папір марки В-55 має у 2.5 раза меншу повітропроникність, у 2.2 раза меншу поверхневу вбирність та на 15 % меншу водопроникність, хоча за масою 1 м^2 зазначені матеріали відповідають рівню 55 ± 2 г/м^2.

Загальний аналіз мікроструктури досліджуваних зразків за збільшення у 200 разів дає змогу зробити висновок, що поверхневе оброблення паперу-основи гідрофобним складом сприяє створенню більш зімкнутої мікропористої структури, яка, за результатами дослідження, є менш проникною для води й повітря порівняно з аналогом.

Світлонепроникність розроблених пакувальних матеріалів перебуває на рівні 74–78.2 % залежно від щільності та маси 1 м^2 паперу й перевищує рівень підпергаменту в середньому на 10 %.

Відносне видовження в момент руйнування у поперечному напрямі для розробленого паперу В-50 становить 7.6 %. Зі збільшенням щільності матеріалу значення показника дещо знижується – до рівня 7.4 та 7.2 % для пакувального паперу марок В-55 та В-65 відповідно. Відносне видовження у машинному напрямі перебуває на рівні 3.3–3.5 %. Для порівння в підпергаменті: 2.6 % – у машинному та 3. 8% – у поперечному напрямах.

Висновки. Розроблені вологоміцні водонепроникні паперові пакувальні матеріали мають підвищені показники водонепроникності, вологоміцності та інші міцнісні та бар'єрні властивості, знижений рівень поверхневої вбирності води порівняно з найближчим за складом і структурою, а також сферою застосування аналогом – підпергаментом.

Ключові слова: паперові пакувальні матеріали, гідрофобний склад, полівініловий спирт, поліамідамінепіхлоргідрин, карбамід.