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PAPER POROSITY STUDIES USING THE SORPTION METHOD

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Abstract. One of the main properties of paper affecting the quality of reproduction is porosity, which depends on many factors, such as properties of raw materials, casting mode. From this point of view it is important to have ideas about the influence of paper composition on their porous structure and it is important to know the dependencies affecting the formation of the porous structure of paper during their manufacture. Papers based on cellulose pulp from the inner layer of mulberry bark were used as an object of study and lint cotton cellulose papers were taken for comparison. In the paper to investigate the porosity of paper in which the composition of cellulose pulp from the inner layer of the bark of mulberry tree twigs, its sorption properties were studied. The structure of a paper sheet contributes to excessive or "selective" absorption of ink into the pores of the paper and thus predetermines the quality of reproduction in the printing process. A large number of experimental methods are now known to determine the porous structure of disperse materials. To investigate the physical structure of paper sheet we studied the sorption of water vapour in a highvacuum sorption apparatus with mercury seals and McBean quartz scales. On the basis of sorption isotherms having S-shape it was determined that high sorption properties have paper sample where in the composition cellulose mass from the inner layer of mulberry tree bark is present, which indicates the presence of disordered amorphous areas where accessibility to water molecules is higher. The porous structure is characterized by such parameters as the specific total volume of pores, the specific surface area of the porous system, which are determined by means of modern measurement tools and computer technology. It was found that in order to obtain a paper whose structure ensured the selective absorption of low molecular weight liquid, it is desirable to change the composition or casting regime.

Keywords: paper, structure, pulp, inner layer of twig bark, mulberry tree, absorption capacity, sorption properties

INTRODUCTION. Paper is one of the basic materials for the printing process, which includes the stages of interaction between ink, paper and the attachment of the ink film to the surface to be printed. The first stage involves the penetration of the ink or its components into the porous structure of the paper. The speed and depth of penetration depend on the pore size of the paper and the viscosity of the ink. In turn, the porosity of the paper is related to the nature of its surface. For example, smooth, high-resolution paper is finely pored, while smooth paper such as newsprint is highly pored. Depending on the porosity of the paper, the interaction between the paper and the ink is different. At the moment of contact with the paper, the ink is pressed into the irregularities of the paper and penetrates into its wide pore mouths as a single system. Once the pressure is released, capillary forces start to operate, causing it to be absorbed.

In the case of coarse-pored paper and low-viscosity ink, it can be absorbed completely, without separating into components. The fine-pored structure of paper promotes selective absorption of low-viscosity components of paints such as oils and solvents. Selective absorption is promoted by adsorption of the binder on the surface of fibers and filler particles. As a result of selective absorption

the pigment concentration in paint layer increases that results in increase of strength of coagulation structure of paint that promotes its fixation. Increased concentration of solid resins leads to the same effect, which is accompanied by a solidification of the binder within the ink layer. For optimum ink-paper interaction it is essential that the composition and viscosity of the ink and its components on the one hand, and the porous structure of the paper on the other, are matched to the printing conditions and the nature of the print product. Selective absorption disturbances caused by a mismatch between paper and ink lead to a variety of process complications and defects. Excessive ink absorption causes the ink to break through to the back of the print, which can lead to the pigment disappearing from the print (when the resin content is low and the absorbency is high). Insufficient solvent absorption impairs ink adhesion and causes smearing and overspray [1].

It follows that one of the main properties of paper which affects the quality of reproduction is porosity, which depends on many factors, such as properties of raw materials, casting regime. From this point of view it is important to have an understanding of the influence of paper composition on their porosity and it is important to know the dependencies affecting the formation of paper porosity during their manufacture [2-3].

At present a large number of experimental methods for determining the porous structure of disperse materials is known. These include liquid, mercury and gas porometry, permeability method, gas dynamic methods, methods of direct observation of pores, capillary and sorption methods [4-6].

In this work, to identify structural changes in cellulose fibres from the inner layer of the bark of mulberry tree branches, taken as an alternative raw material to the scarce wood for paper production, the study was carried out by sorption methods [7-8].

In order to achieve the goal, the following tasks were solved:

- Papers based on cellulose pulp from the inner layer of mulberry bark were obtained under a certain technological regime;

- Physico-mechanical properties of paper samples were studied;

- Using sorption method the porosity of paper on high-vacuum sorption unit with mercury seals and quartz McBean scales was determined,

- parameters of capillary-porous structure of samples were determined by BET theory;

- the characteristics of the obtained materials have been studied and recommendations for their application have been proposed.

MATERIAL AND METHODS. Papers based on cellulose pulp from the inner layer of mulberry bark and for comparison cotton pulp papers from lint were used as an object of study. The properties of the paper samples examined according to the standard methodology [9] are inserted in Table 1.

Toperties of paper samples with unterent casting options							
Composition of paper	Whiteness,	Destructive	Breaking	Fracture resistance,			
XC:TC, %	%	force, N length, m		number of			
				twists/rebounds			
100:0	82	49,1	4180	280			
0:100	74	60,1	5110	550			

Properties of paper samples with different casting options

Table 1

RESULTS AND DISCUSSION. Analyzing the properties of the paper samples (Table 1) it was found that the breaking load defined according to GOST ISO 1924-1-96 characterised the maximum

force the paper sample was able to withstand before breaking. Using the results of the test, we calculated the tensile length of a strip of paper which broke under the action of its own mass. The increase in the mechanical strength of the paper tested, relative to the strength of cotton pulp, can be explained by the fact that the formation of a mass of fibrillated fibres of the inner bark layer of mulberry branches contributed to a better mechanical interweaving between the different fibres.

Paper, which is a polymer with hydroxyl groups, is hygroscopic and therefore absorbs moisture from the atmosphere until it reaches an equilibrium state relative to ambient air. In this connection it is of great interest, both from a scientific and practical point of view, to study the sorption of low molecular weight liquid, particularly water, by cellulose [10-12].

The sorption method used in this work is based on the condensation of gases (adsorbates) on the open (accessible to gas molecules) surfaces of adsorbents. This method, as well as the mercury porometry method, is suitable for the study of materials with a developed porous structure, complements the mercury porometry method in the micropore area, the most difficult for the porometric analysis, allows to reliably determine the specific surface of the porous structure.

Water vapour sorption was carried out on a high-vacuum sorption unit with mercury gates and McBenne quartz scales. The vacuum part of the unit is designed for generation of residual air pressure of 10-3Pa, and in the working part sorption measurements are directly performed. Before carrying out the experiments the polymers under study and water were anhydrated beforehand at a residual pressure of 0.013Pa to constant mass. The solvent was fed to the sample in successive increasing portions. The total relative error of the value of the equilibrium amount of absorbed water per 1 g of polymer did not exceed 3%, the relative systematic error in the vapour pressure measurement was 0.1%.

The sorption values in the initial stage of the process (Fig. 1) are the result of the binding of water molecules and the most accessible primary hydroxyl groups of the elementary chain of cellulose macromolecules, which are located in the amorphous regions and on the surfaces of crystallites. The intensity of sorption is explained by the amount of bound water in disordered (amorphous) regions where the intermolecular interaction is weak. The sorption capacity can be used to judge the degree of crystallinity, which is inversely proportional to it.

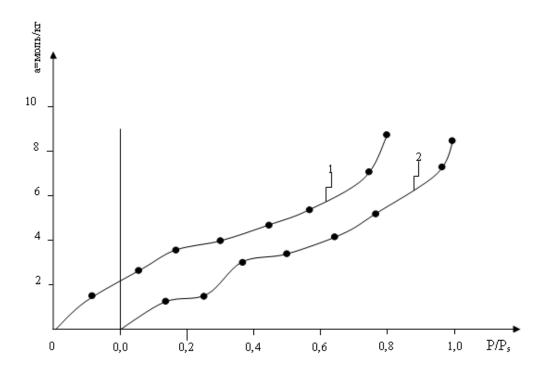


Figure.1. Isotherms of water vapour adsorption on the paper samples tested: 1 - mulberry cellulose based paper, 2 - cotton cellulose based paper

Comparing the adsorption isotherms with each other (Fig. 1) we can say that, relative to cotton cellulose paper, the paper studied has a sorption capacity due to the presence of amorphous areas.

The porosity of the structure is characterized by such parameters as specific total volume of pores, specific surface of the porous system, which are determined by means of modern measuring tools and computer technology.

One way to determine the size of pores is to study the adsorption of water vapor, described by the polymolecular theory of adsorption accompanied by capillary condensation, BET theory. BET theory establishes a relationship between specific adsorption a and vapour pressure p [13-14].

In this paper on the basis of water vapour sorption isotherms (Fig.1) using BET theory parameters of capillary-porous structure of samples were determined: monolayer capacity (am), specific surface area (S), adsorption saturation (as), total pore volume (W₀), mesopore Wme=Vs-W₀ and adsorption saturation volume (Vs). The results of the calculations are presented in Table 2.

Table 2

		Composition	Capacity	Specific	Adsorption	The	The volume	The volume
		of paper	of the	surface	of	volume	of	of saturation
N⁰	No		mono-	area S _{уд} ,	saturation	of total	Mesopore	V_{s} ·10 ³ ,
		layer $a_{\rm m}$,	m²/g	$a_{\rm s}$, mol/kg	pore	W_{Me} . 10 ³ ,	m ³ /kg	
			g/g			$W_0 \cdot 10^3$,	m³/kg	
						m ³ /kg		
	1	TC-100%	1,969	128,01	8,6	0,1052	0,0501	0,155

Capillary porous structure parameters of the samples from water vapour sorption data

2	XC-100%	1,720	111,83	8,5	0,0958	0,0572	0,153
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From the values of the monolayer's capacity am determined the amount of adsorbate contained in the completely filled in monolayer of molecules on the surface of a solid, and calculated the specific surface Sd.

The specific surface of paper is the total surface area of a unit of its mass or volume and, like paper porosity, characterized the structure of a paper sheet. To calculate the specific surface area of sorbents, which are characterized by S-shaped sorption isotherms, the BET equation was used.

As can be seen from Table 2, the use of cellulose pulp from the inner layer of mulberry bark affected the value of capillary-porous structure parameters of the sample. When comparing the samples capillary-porous structure parameters increase: specific surface area - from 111.83 to 128.01 m2/g, while the paper of cotton cellulose has 89.34 m2/g, and the total volume of mesopores - 0.05 in cotton 0.11 m3/kg [11].

According to the classification of academician M.M. Dubinin the specific surface of macropores makes about 0.5 - 2.0 m2/g, of mesopores - from 10 to 500 m2/g, of micropores can reach 1000-2000 m2/g with the size of pores less than 2 nm [15]. Based on the results obtained for specific surface values it can be said that the size of mesopores is in the range from 18 to 28 nm.

Total pore volume in cellulose materials was used to analyse the degree of absorption by the amount of water absorbed by the fibres by filling the pores and capillaries. When cellulose pulp from the inner bark layer of mulberry tree branches the total pore volume increases from 0.10 m3/kg, which is characteristic according to the data of Tager A.A., Tsilotkin M.V., Makovskaya E.B. The average value of pore volume in cellulose materials is about 3% of the total volume of the material.

CONCLUSION

Thus, the effect of the composition, namely the use as an alternative raw material in the production of paper pulp from the inner layer of bark of mulberry trees on the specific surface area, the total volume of pores and the volume of saturation was studied.

The use of cellulose pulp from the inner layer of mulberry bark in paper pulp increased the mechanical strength of the paper sheet by 22% compared to paper made from cotton pulp.

Based on sorption isotherms having an S-shape, it was determined that the sorption properties of the paper sample under study, due to the presence of amorphous areas, where the availability to water molecules is higher. Paper where cotton cellulose is used has a relatively low sorption capacity due to the degree of crystallinity.

In order to obtain a paper whose structure has sufficient absorbency, it is desirable to change the composition stock or the mode of casting, for high-quality printing without disturbing the selective absorption, which leads to various complications of technology and defects.

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