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Starch Modification to Ensure Resource Savings and Environmental Safety in the Production Cardboard from Waste Paper

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ABSTRACT

Development of new and modification of existing chemicals, which act not only as binders, but also provide increased retention of fiber and other pulp components on the paper machine grid, accelerate pulp dehydration, and provide special properties (moisture resistance, heat resistance, improvement of other technical characteristics of paper and cardboard) of paper and cardboard, is an important and urgent task of chemical technology and ecology. This paper presents results of the corn starch modification with epoxypropyltriethanolammonium chloride, hexamethylolmelamine and hexamethylenetetramine. Modified starches provide the necessary strength indicators of cardboard from waste paper and low turbidity of wastewater. The obtained starches can be used in mills that use low-quality waste paper for the production of cardboard and paper products with the aim of saving fiber, reducing wastewater pollution and as a result reducing the negative impact on the environment.

Keywords: starch, modification, cardboard, wastewater, turbidity.

INTRODUCTION

The volumes of paper and cardboard production in the world are growing annually. At the same time, the practice of using secondary raw materials – waste paper – is expanding. In general, the production of paper and board from secondary fibers is growing at a fairly fast pace – about twice as fast as the production of paper from primary fiber, which is due to both economic and environmental factors. Despite this, the increase in the use of waste paper is restrained, on the one hand, by the gradual deterioration of secondary fiber characteristics, and on the other, by the constant increase in requirements for the quality of final products (Salam et al., 2013). Mills that process waste paper are characterized by an increased content of polluting components in wastewater, which have a dangerous impact on the environment (Jung and Kappen, 2014; Man et al., 2018). Wastewater mixed with wastewater from other chemical industry enterprises has a detrimental effect on natural water bodies. The efficiency of water purification depends on the treatment method (Trus et al., 2020; Radovenchyk et al., 2021).

According to its composition, waste paper mass is a polydisperse system with an increased content of small fibers, which have a weak ability to form intermolecular hydrogen bonds and during the formation of a paper sheet, they reduce the mechanical adhesion of fibers, which in general leads to a decrease in the strength of the finished product (Viana et al., 2018). At the same time, the pollution of wastewater due to fiber leaching in paper formation process taken place (Kamali and Khodaparast, 2015). It is possible to improve the quality of cardboard and paper products from waste paper by adding cellulose from non-wood plant materials, however, to obtain it, significant investments are needed to establish technological processes (Deykun et al., 2018; Trembus et al. 2018; Trembus et al., 2022). One of the decisive conditions for improving the quality of finished products made from waste paper is the use of chemicals that ensure the increase in the efficiency of the use of waste paper, the reduction of pollution of wastewaters and, thereby, enable resource-saving production technologies.

Today, various types of natural and synthetic chemicals are used in the production of various types of paper and cardboard. The consumption of chemicals is quite large in modern technological processes, which subsequently affects the cost of finished products. In addition, it is worth noting that the degree of retention of such fillers in the paper pulp usually does not exceed 80%, which leads to the pollution of sub-grid water. An urgent task is to reduce the consumption of polymeric substances by developing new polymeric compositions capable of solving the problem of hydrophobization and strengthening, as well as acting as an alternative to products already available on the market. As strengthening agents for paper and cardboard, starches remain undisputed leaders in the global practice of pulp and paper production (Li et al., 2019). The use of native starch is complicated by the fact that it is characterized by the high viscosity of its solution and the tendency to retrogradation (Wang et al., 2015). Therefore, modified starches have gained practical application. The presence and chemical properties of hydroxide groups, which are reaction centers in the starch molecule, determines the direction of their modification. C-OH groups easily interact with aldehyde groups or epoxy rings, resulting in cationization of starches. In addition, it is possible to use phosphorylation to modify starches. Sodium salts of phosphoric acid are most often used for this purpose, since in the process of heating at low pH values water is separated from the polysaccharide and carbonization of starch occurs (Mahlow et al. 2016).

The cationization process is considered to be the most widespread and promising for starch modification (Prado and Matulewicz, 2014). In the case of amination of starches, an increase in the stability of the obtained pastes, which also acquire resistance to retrogradation is observed. At the same time, colloidal systems are formed, stabilized due to the surface positive charge on the surface of starch micelles. Quaternary ammonium salts or quaternized starches are used in the preparation of strongly cationized starches (Balsamo et al., 2011; Liu et al., 2017). Most often, secondary or tertiary amines (dimethyl- or trimethylamine) are used for this, which are not produced in Ukraine and are imported from abroad. This problem can be solved by using more available amines or reagents to modify starch. The aim of the work is to develop methods of effective modification of native starch to increase the efficiency of its use in order to ensure effective retention of fiber on the grid and physical and mechanical indicators of cardboard during paper recycling.

MATERIALS AND METHODS

Corn starch was used for modification. Characteristics of corn starch are given in Table 1. The method of obtaining KROHUR cationized starch is as follows: concentrated hydrochloric acid was added to a solution of hexamethylenetetramine in water (concentration 20%) to reach pH 1.0 and then the solution was boiled for 3 hours. Under these conditions, the pH value of the solution changed and reached 5.0 due to the decomposition of hexamethylenetetramine and the formation of oxymethyleneamines, which have more basic properties than the original compound. The resulting solution was diluted with deionized water and heated to 90°C, after which a suspension of starch in cold water was added to the solution at constant stirring in an amount that made it possible to obtain a solution of modified starch in water with a concentration of 6%. The resulting mixture was kept at a temperature of 90°C for 30 minutes at constant stirring. The mass of hexamethylenetetramine used in the experiment was 10–40% of the mass of the starch to obtain

Table 1. Characteristics of corn starch

Indicator	Description/value
Appearance	Homogeneous powder
Color	White with a yellowish tint
Scent	Starch smell
Moisture, % no more	13
Ash content, % no more	0.30
Mass fraction of protein, % no more	1.0
Mass share of SO2, % no more	0.08
The number of grains per 1 dm^3, pcs, no more	500

a nitrogen content in cationized starch from 3.6 to 11.4%. The method of obtaining KROHMEL cationized starch is as follows: the calculated amounts of melamine (40 g) and paraformaldehyde (72 g) were added to the calculated volume of water (200 cm^3). The mixture was heated at constant stirring to a temperature of 80 °C. After dissolving melamine in water, enough water was added to the formed hexamethylolmelamine to obtain a paste with a cationic starch concentration of 6% after adding starch. The temperature of the solution was raised to 90–95°C, and a suspension of starch in cold water was added in small portions. After adding all the starch, the mixture was stirred for 2 hours at a temperature of 90–95°C to complete the cationization process.

The method of obtaining KROHAM cationized starch is as follows: 10.5–14.4 g of epichlorohydrin was added to 16.9–23.1 g triethanolamine solution. The mixture was kept at room temperature for 5 days. After the crystallization of the epoxypropyltriethanolammonium chloride, distilled water was added in the amount of 800 cm3 and heated to 90°C, and a suspension of corn starch in cold water was slowly added (with a dry substance content of 25.2 g per 200 cm^3 of water), controlling that the temperature of the mixture did not fall below 85 °C. As a result, a paste of cationized starch was obtained.

Modified starches were used to obtained samples of cardboard. Waste paper such as corrugated cardboard from unbleached cellulose, container and box cardboard with color printing and used newsprint paper were used as a raw material for cardboard production. The degree of grinding of the waste paper mass was 35 °SR. Wastewater from the cardboard formation process was collected and analyzed.

In order to reduce the volume of the experimental load, a full factorial design of 2^2 type was used to investigate the effect of modified starch consumption and nitrogen content on the strength properties of cardboard samples. The following variables (X_i) were chosen as factors affected the strength of cardboard: X_1 – nitrogen content in starch, %; X_2 – consumption of starch, %. Data for the implementation of full factorial design are given in Table 2.

To reproduce the experimental data, a second-order polynomial was used for two independent variables:

$$Y_i = b_0 + b_1X_1 + b_2X_2 + b_3X_1X_2 + b_4X_1^2 + b_5X_2^2 \quad (1)$$

where: Y_i – indicators of the obtained products; b_0, b_1, b_2, b_3, b_4, b_5 – regression equation coefficients; X_1 and X_2 – values of process parameters.

RESULTS AND DISCUSSION

As a result of processing experimental data on the effect of nitrogen content in starch and starch consumption on strength indicators, a regression equation was obtained that adequately describes the process of obtaining cardboard:

- for KROHUR:

$$Y_1 = 243 + 1.933X_1 + 118.71X_2 - 0.63X_1X_2 - 0.046X_1^2 - 28.59X_2^2 \quad (2)$$

$$Y_2 = 2.15 + 0.29X_1 + 0.29X_2 + 0.06X_1X_2 - 0.01X_1^2 - 0.11X_2^2 \quad (3)$$

- for KROHMEL:

$$Y_1 = 78.72 - 3.28X_1 + 486.06X_2 + 2.08X_1X_2 + 0.09X_1^2 - 166.65X_2^2 \quad (4)$$

$$Y_2 = - 0.33 + 0.07X_1 + 6.3X_2 + 0.02X_1X_2 - 0.01X_1^2 - 2.19X_2^2 \quad (5)$$

Table 2. Data for implementation of full factorial design

Factors (x_i)	Levels of factors	
	(+1)	(–1)
KROHUR		
X_1 – nitrogen content in starch, %	11.4	3.6
X_2 - consumption of starch, %	1.5	0.7
KROHMEL		
X_1 – nitrogen content in starch, %	19.1	6.1
X_2 - consumption of starch, %	1.5	0.7
KROHAM		
X_1 – nitrogen content in starch, %	3.5	1.7
X_2 - consumption of starch, %	1.5	0.7

- for KROHAM:

$$Y_1 = 134.14 + 6.21X_1 + 382.21X_2 + 30.57X_1X_2 - 4.47X_1^2 - 169.72X_2^2 \quad (6)$$

$$Y_2 = 2.73 - 0.084X_1 + 0.712X_2 - 0.009X_1X_2 + 0.029X_1^2 + 0.44X_2^2 \quad (7)$$

where: Y_1 – absolute resistance to compression of cardboard, *N*; Y_2 – compressive strength in the transverse direction of cardboard, kN/m.

The value of the correlation coefficients for the mathematical models (2–7) is close to 1, which indicates that they are adequate for their use to describe the process of obtaining cardboard samples from wastepaper using synthesized cationic starches. The results of predicting the properties of cardboard using the obtained mathematical models are presented in Figures 1–3. The presented results indicate that the use of synthetic cationic glues KROHUR, KROHMEL and KROHAM based on corn starch has a positive effect on the quality indicators of cardboard from waste paper. An increase in the consumption of starches in all the studied series of samples leads to an increase in the values of absolute resistance to compression and compressive strength in the transverse direction. An increase in the nitrogen content in the received cationic starches has a similar positive effect on strength indicators. Obviously, the presence of nitrogen contributes to the formation of a larger number of hydroxyl bonds in the interfiber space of a paper sheet.

In order to assess the feasibility of carrying out the cationization of starches according to the methodology developed by us, a series of experiments was performed with the production of cardboard samples under the same conditions, but without the use of starch and with the application of traditional industrial starches. For comparison, unmodified corn starch, cationized starches Cationamyl and Cerezan were used. The results are shown in Figure 4. It should be noticed that the time of dehydration of the mass on the grid of the machine was almost the same and was within 12–13 s.

The data show that at a consumption of 0.7%, native starch and Cationamyl have no effect on the cardboard parameters. Further increase in consumption of these starches to 1.5% allows to increase the absolute resistance to compression by 1.1 times when using corn starch and by 1.25 and 1.3 times when using Cationamyl and Ceresan, respectively (Fig. 4a). The use of traditional reinforcing additives has the same effect on the compressive strength in the transverse direction of cardboard (Fig. 4b). The results of the study of the strength parameters of cardboard with a consumption of starches of 0.7% indicate that at this value the absolute resistance to compression is approximately within the same limits for all samples, while the compressive strength in the transverse direction is influenced by the nitrogen

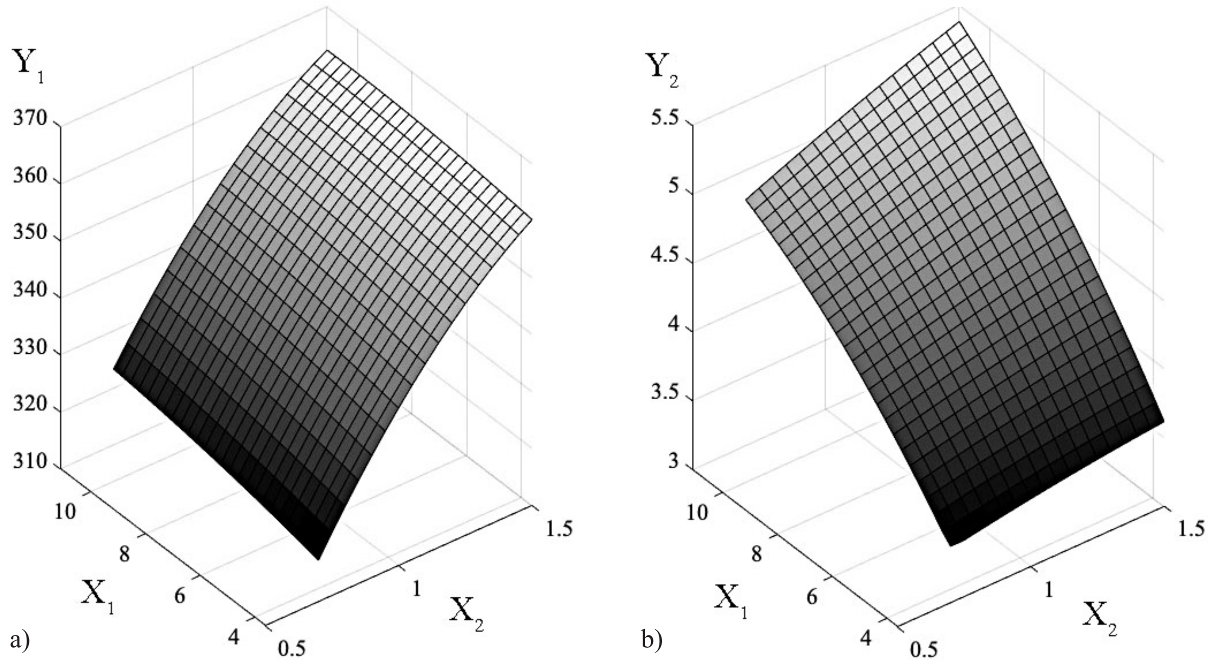

Figure 1. 3D surface predictions of cardboard properties using KROHUR: absolute resistance to compression (a) and compressive strength in the transverse direction (b)

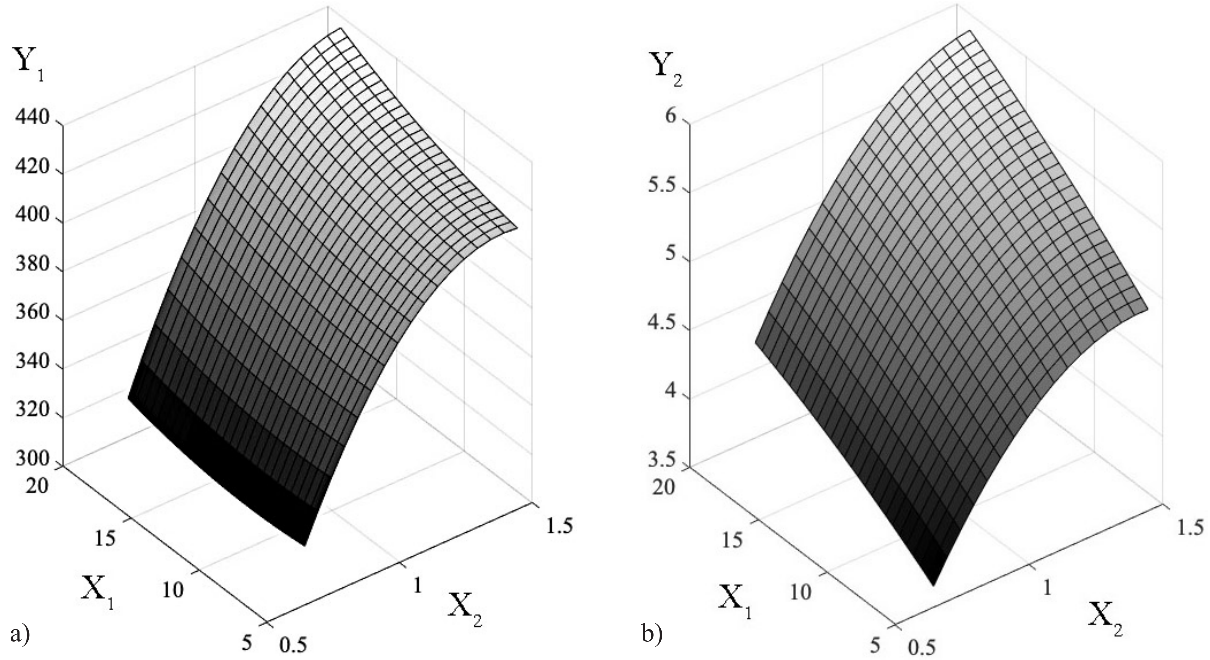

Figure 2. 3D surface predictions of cardboard properties using KROHMEL: absolute resistance to compression (a) and compressive strength in the transverse direction (b)

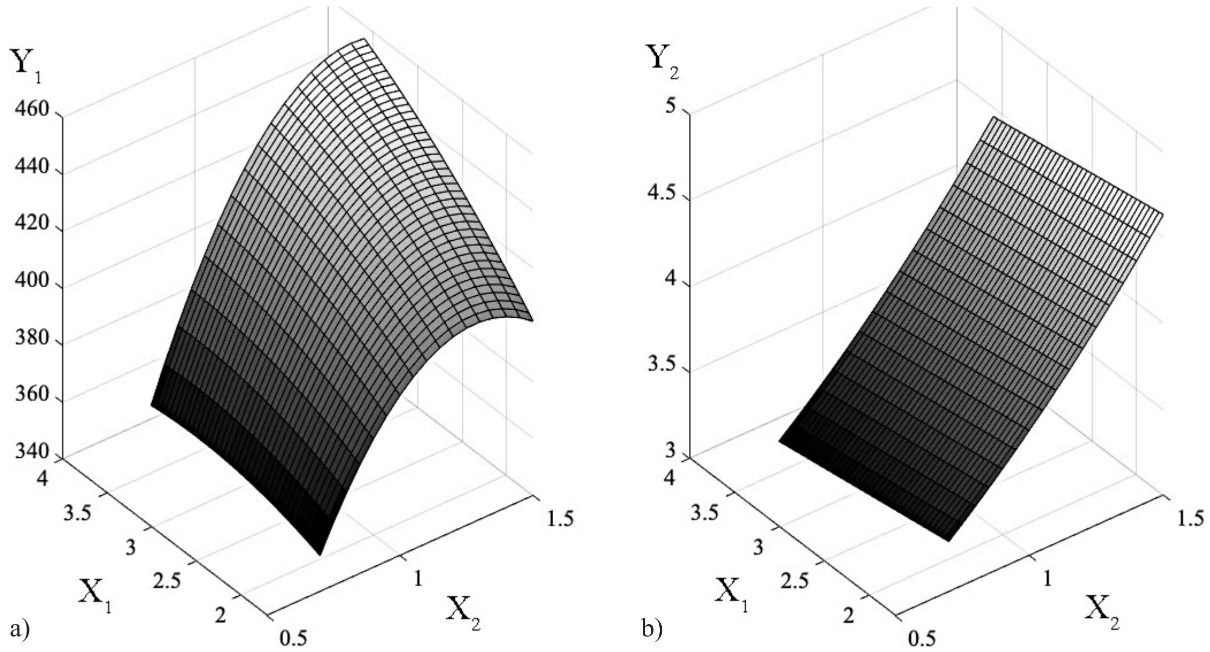

Figure 3. 3D surface predictions of cardboard properties using KROHAM: absolute resistance to compression (a) and compressive strength in the transverse direction (b)

content in the synthesized starches. The effect of starches modified with epoxypropyltriethanolammonium chloride and hexamethylenetetramine on the absolute resistance to compression can be compared with the values obtained with Cerezan. Starch treated with hexamethylenetetramine corresponds to native corn starch and is inferior to Cationamyl and Cerezan in terms of absolute resistance to compression, and the nitrogen content does not play a significant role.

However, in the case of compression force in the transverse direction, increasing the nitrogen content to 11.4% allows to improve this indicator by 15%. According to the increase in efficiency in increasing strength indicators, the obtained starches are arranged in the following

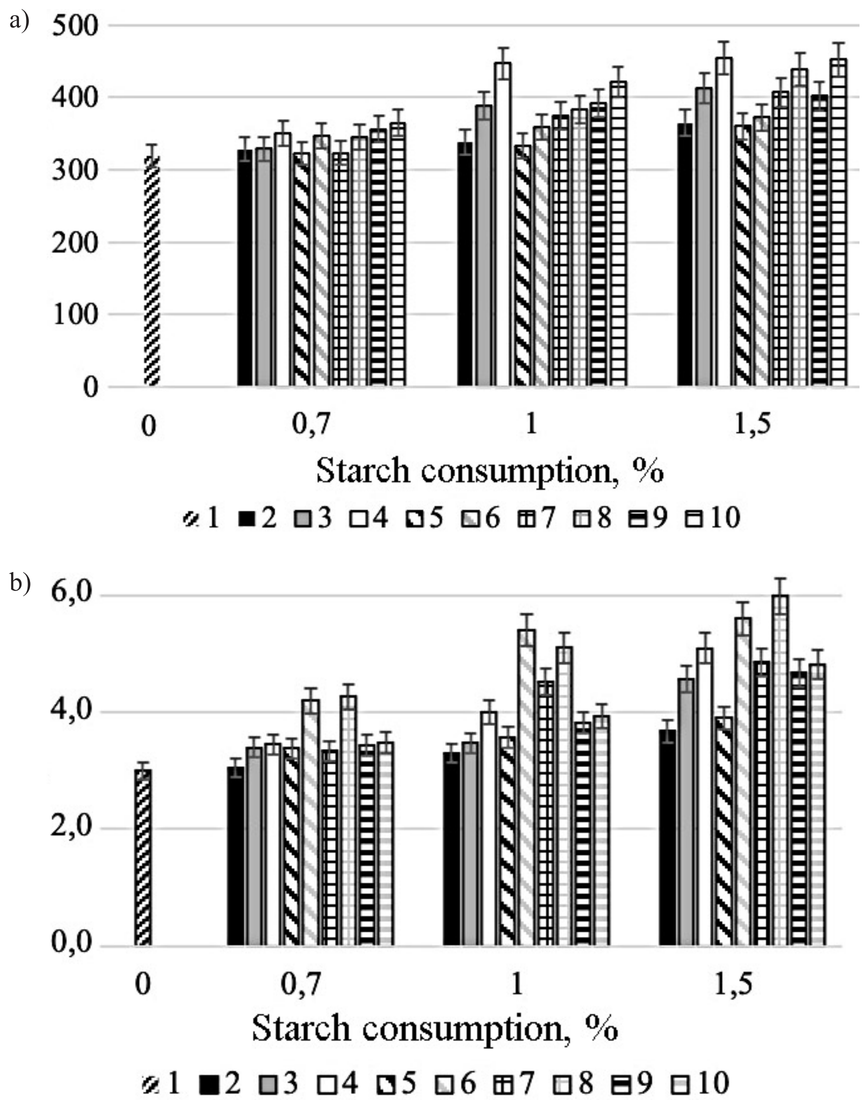

Figure 4. The influence of starch consumption on the strength properties of cardboard from waste paper: a – absolute resistance to compression, b – compressive strength in the transverse direction of cardboard; 1 – cardboard without starch, 2 – native corn starch; 3 – Cationamyl; 4 – Cerezan; 5 – KROHUR with a nitrogen content of 3.6%; 6 – KROUR with a nitrogen content of 11.4%; 7 – KROHMEL with a nitrogen content of 6.1%; 8 – KROHMEL with a nitrogen content of 11.2%; 9 – KROHAM with a nitrogen content of 1.7%; 10 – KROHAM with a nitrogen content of 3.5%

sequence: KROHUR – KROHMEL – KROHAM. Regarding the influence of starches on the retention of mass on the grid, it can be noticed that KROHUM with a nitrogen content of 3.6% does not differ from native corn starch and is inferior to cationic Kationamyl and Cerezan (Table 3). However, an increase in the nitrogen content to 11.4% leads to an improvement in the adsorption interaction of starch with cellulose fiber, as a result of which the degree of its retention increases to 50%, which exceeds the value for native starch by two times, but is still inferior to the other two industrial starches. The use of KROKHAM, obtained by modification of starch with epoxypropylenetriethanolammonium chloride, allows to reduce significantly the turbidity of wastewaters to 26 mg/dm^3, with a starch consumption of 1%. Under these conditions, KROHAM provides mass retention on the grid even more effectively than strongly cationic Cerezan.

The analysis of the obtained results shows that the differences between the starches obtained by different methods of modification are very significant in influencing the degree of retention in the composition of the cardboard. The degree of retention of modified starches increases with an increase in their nitrogen content and an increase in the consumption of starch in the paper composition.

Table 3. The influence of starch consumption on the quality of wastewater in the production of cardboard from waste paper

Starch	Nitrogen content in starch, %	Consumption of starch, %	Turbidity of wastewaters, mg/dm^3	Carbohydrate concentration in wastewaters, %	Degree of retention of starch in mass, %
Without starch	-	-	160.4	-	-
Native corn	-	0.7	154.9	31.4	15.3
		1.0	103.8	38.5	15.9
		1.5	97.9	51.4	20.1
Cationamyl	-	0.7	158.6	8.9	73.3
		1.0	74.5	9.4	74.6
		1.5	67.3	12.4	75.6
Cerezan	-	0.7	144.6	6.4	77.5
		1.0	64.3	8.1	79.4
		1.5	32.9	10.6	80.5
KROHUR	3.6	0.7	155.2	33.4	14.5
		1.0	150.1	42.1	16.3
		1.5	83.7	45.7	18.4
	11.4	0.7	151.2	24.5	35.0
		1.0	92.1	29.6	40.6
		1.5	75.6	31.4	50.3
KROHMEL	6.1	0.7	150	10.7	57.6
		1.0	93	11.8	66.2
		1.5	85	12.9	73.7
	19.1	0.7	142.6	9.1	65.0
		1.0	63.1	10.7	74.0
		1.5	44.5	12.2	75.8
KROHAM	1.7	0.7	120.1	7.4	73.9
		1.0	43.5	8.9	77.0
		1.5	27.8	11.7	77.8
	3.5	0.7	115.7	6.3	77.3
		1.0	44.8	9.2	78.9
		1.5	25.6	10.1	80.9

CONCLUSIONS

The processes of modification of starches using reagents available in Ukraine – hexamethylenetetramine, melamine, epichlorohydrin and triethanolamine – were studied. Modification of starch with hexamethylolmelamine, epoxypropyltriethanolammonium chloride leads to improvement of cardboard quality when modified starches are added to the waste paper mass. These modified starches provide strength parameters of paper at the level of cationic starch Kationamyl and strong cationic starch Cerezan. They improve mass retention on the mesh and, according to this indicator, exceed the values for traditional starches.

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