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Issue **Article**

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APPLICATION OF PHOSPHATE STARCH AS INK THICKENER

Abstract*: In the work possibility of starch modification by phosphatic compounds and study of applying of obtained preparations, as thickeners in printing by active dyes on cotton fabrics is learned. Let's mark, that the degree of thickening is various for various concentrations of polymer and 4 % of masses reaches maximum rating for solutions with concentration of starch. It's detected, that the effect of thickening starts at some extreme value of concentration of modifying agent.*

Temperature effect on rheological behavior of chemically treated solutions of starch is also investigated. The time of deformation relaxation of polymers is decrease with decreasing of characteristic viscosity, and, therefore, at the given degree of polymerization at a decrease of concentration of polymer in solution.

Key words*: dynamic viscosity, modifier, yield point, degree of thickening, concentration, thickening.*

Language*: English*

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Introduction

The relevance of the search for new ways of chemical, physical and mechanical modification of starch in order to improve the technological properties and reduce the consumption of raw materials is due to the wide use of this natural polysaccharide in various industries, in particular in the textile industry for thickening printing inks [1, 2, 3].

Due to the widespread use of active dyes in textile printing, it has become difficult to provide the textile industry with appropriate thickeners. Therefore, in many scientific studies, work is being carried out to find new types of thickeners that fully replace the classic thickener for active dyes, such as sodium alginate [4–12]. The scarcity and high cost of this thickener currently make this topic relevant. Work is carried out mainly in the direction of replacing sodium alginate with water-soluble synthetic high-molecular compounds. However, so far not a single product has been produced on an industrial scale in our Republic. Starch continues to occupy a leading position among thickeners, and various forms of starch are also used, which have significantly improved properties compared to natural ones.

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The purpose of this work was to study the possibility of modifying starch with phosphate compounds and to study the use of the obtained preparations as thickeners in printing with active dyes on cotton fabrics.

In table. 1 shows the values of the maximum and minimum dynamic viscosities of starch solutions of various concentrations before (hini) and after (hA) their chemical treatment with phosphate compounds.

Table 1. Effect of Modifier Concentration on Dynamic Viscosity and Yield Strength of Starch Phosphate Solutions

C, % mas.		Dynamic viscosity, Pa·s				Yield strength, Pa		Degree of thickening $h_A/h_{исх}$
		original		after modification				
		$Д_г$=1,3 c^{-1}	$Д_г$=1310 c^{-1}	$Д_г$=1,3 c^{-1}	$Д_г$=1310 c^{-1}	original	after modification	
4	10	0,145	0,043	2,167	0,064	110	265	13,8
	15	0,166	0,051	2,440	0,076	230	310	12,3
	20	0,183	0,058	3,275	0,089	315	375	12,1
	25	0,194	0,067	3,640	0,105	380	420	12,0
5	10	0,936	0,076	13,760	0,126	420	490	11,45
	15	1,015	0,094	14,210	0,137	470	520	10,25
	20	1,235	0,126	16,720	0,154	435	615	9,40
	25	1,464	0,154	18,915	0,166	520	690	8,16
6	10	1,672	0,215	26,440	0,185	540	750	7,60
	15	1,865	0,236	26,810	0,197	575	785	5,43
	20	2,025	0,254	26,925	0,203	710	810	5,21
	25	2,345	0,287	27,315	0,218	890	920	5,05
7	10	2,815	0,364	28,175	0,226	1030	1150	4,25
	15	3,140	0,396	28,240	0,237	1070	1230	3,68
	20	3,870	0,417	28,570	0,241	1090	1290	3,21
	25	4,365	0,445	28,683	0,244	1110	1340	3,07
8	10	9,750	0,463	29,640	0,245	1170	1430	2,60
	15	10,215	0,485	29,870	0,276	1220	1520	2,43
	20	10,840	0,496	29,915	0,283	1260	1610	2,26
	25	11,250	0,514	30,116	0,296	1320	1660	2,14

As can be seen from the table, the formation of starch phosphates in a heterogeneous liquid-phase system causes a significant increase in the maximum dynamic viscosity (Dg = 1.3) and yield strength (□T) for all studied concentrations. The minimum viscosity does not change significantly. Note that the degree of thickening is different for different polymer concentrations and reaches its maximum value for solutions with a starch concentration of 4% wt.

It is known that under the action of shear deformations with low velocity gradients on systems formed by anisotropic particles, such particles can be completely misoriented, and under the action of high-speed shear, they can be completely oriented. It was of interest to study the effect of modifier concentration on the rheological behavior of starch solutions of various concentrations. On fig. 1 shows the dependences of the maximum dynamic viscosity of starch phosphate solutions with concentrations of 4; 5 and 6% wt. at different modifier concentrations. As can be seen from the figure, the thickening effect begins at a certain critical value of the modifier concentration.

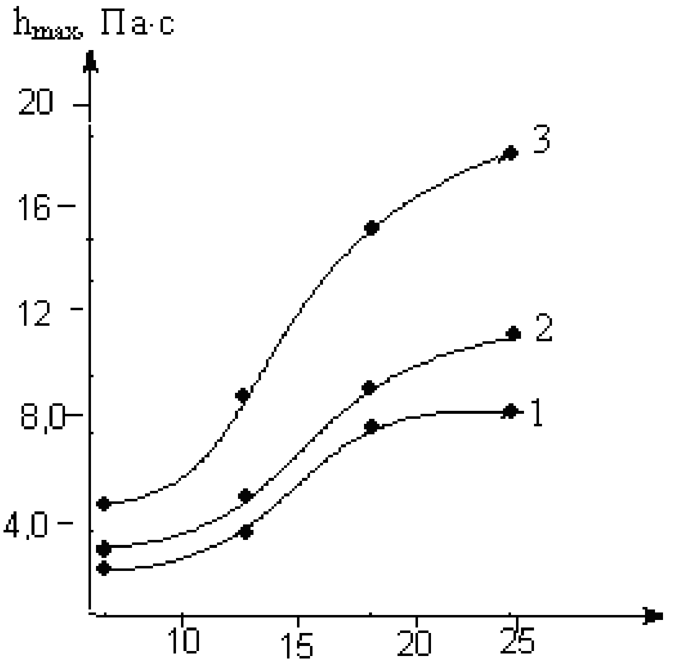

Fig. 1. Flow curves of 4% aqueous solutions of starch: initial (1), processed in an activator at n = 3500 without a modifier (2) and in the presence of a modifier (3)

This fact can be explained as follows. The nature of the rheological curves for aqueous solutions of starch is determined by the ratio in the solution of the molecularly dissolved part of the polymer and the amount of the colloidal dispersed phase. It can be assumed that the action of shear forces causes the destruction of the molecular network of entanglements, the orientation of released macromolecules, and the appearance of new supramolecular formations. The shift-induced phase transformations in the system lead to a change in the quantitative ratio of the molecularly dissolved and colloidal-dispersed phases in favor of the latter. An increase in the proportion of the colloidal-dispersed phase and an increase in the interaction between oriented particles determines the characteristic, almost vertical arrangement of the flow curves of chemically thickened starch solutions. In other words, the chemically thickened starch solutions exhibit a more pronounced viscosity anomaly than the initial solutions. This rheological behavior of solutions is undesirable when used as thickeners for printing compositions.

The authors have made attempts to chemically modify starch thickeners. For this purpose, special chemical modifiers were selected that prevent the dense packing of starch chains deployed in the flow, and thereby reduce the proportion of the colloidal dispersed phase. In this case, the system, as can be seen from Fig. 3 becomes more plastic, the slope of the yield curve decreases (Fig. 3, curve 3). Modifiers were introduced into cold starch solutions before their chemical treatment in the amount of 0.1-0.2%. There is reason to believe that the chemical treatment of the solution in this case not only ensures a good distribution of the modifier and a high level of homogeneity of the entire system, but also catalyzes the chemical interaction of the low molecular weight modifier with the polymer.

In this work, the effect of temperature on the rheological behavior of chemically treated starch solutions was investigated. On fig. 4 shows the flow curves of starch solutions treated at 20, 40 and 60 °C.

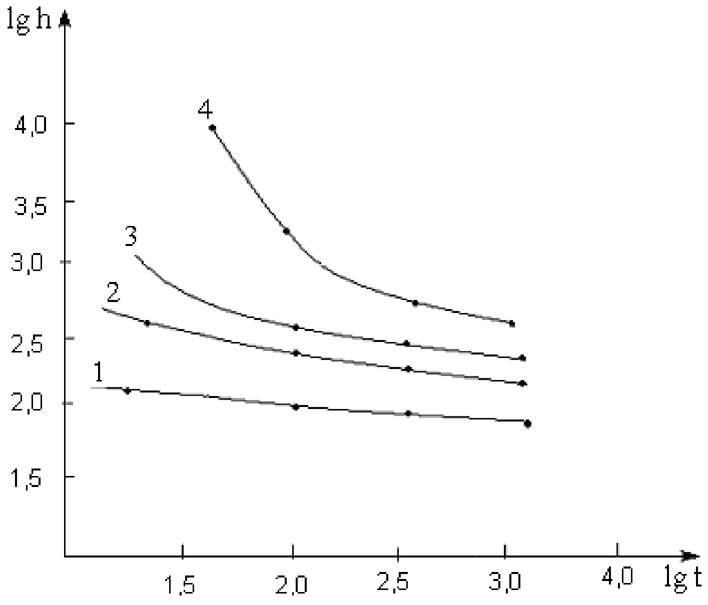

Fig. 2. Flow curves of 4% aqueous solutions-suspensions of starch subjected to chemical treatment at various concentrations of the modifier: 1(10); 2(15); 3(20); 4(25)

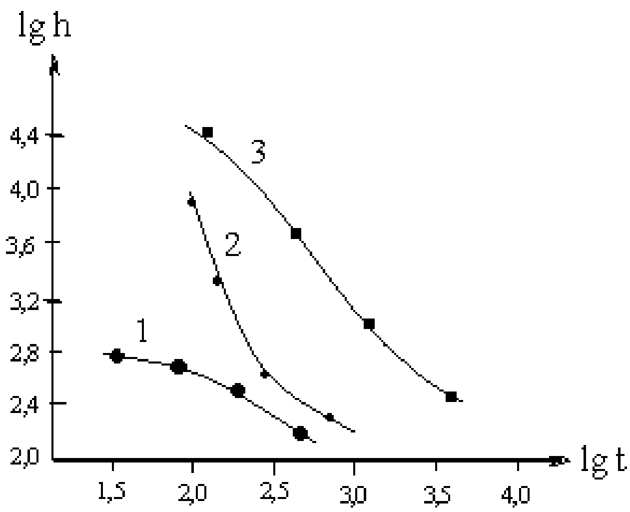

Fig. 3. Flow curves of 4% aqueous solutions of starch: initial (1), processed in an activator at n = 3500 without a modifier (2) and in the presence of a modifier (3)

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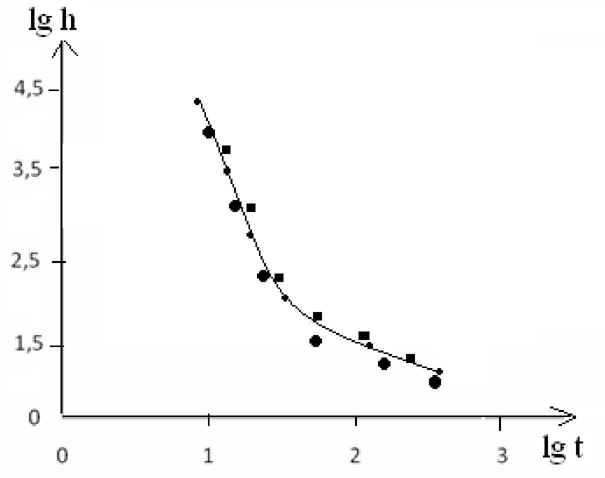

Fig. 4. Dependences lgh = f(lgt) for 4% aqueous solutions of starch treated in an activator at different temperatures: 20 °C(•), 40 °C(■) and 60 °C (○)

As we see from fig. 4, a change in the process temperature within the specified limits does not cause a noticeable change in the rheological behavior of the treated solutions. This experimental fact is difficult to explain theoretically. Perhaps this is due to the compensation of various effects that affect the probability of orientation processes in opposite ways: an increase in temperature leads to an increase in the mobility of macromolecules, on the one hand, and to a weakening of fixing hydrogen bonds, on the other. In practical terms, the experimentally obtained independence of the thickening effect from temperature eliminates the need to exercise strict control over the temperature of the processed mixture when preparing thickeners from starch by a chemical method. Chemically modified starch-based thickeners have been tested in the printing of cotton fabrics with active dyes.

Table 2. Influence of the nature of the thickener and the method of its modification on the technical results of cotton fabrics when printed with bright red ostazine ZB-Ash

Thickening name	Way modifications	Thickener concentration, g/l	Intensity coloring K/S	Color fastness, score			The degree of fixation of the active dye, %
				to laundry N 2	к поту	to dry friction	
Starch silicate		70	17,0	4/4/4	4/4/4	5	82,5
Starch	non-modified	80	16,2	4/4/4	4/4/4	5	68,0
Phosphate starch	chemically modified	40	22,8	5/5/5	5/4/5	5	92,0

In table. Figure 2 shows for comparison the technical results of printing cotton fabrics with bright red ostazine ZB-ASh using various thickeners for the preparation of printing inks. The use of starch-metasilicate and unmodified starch does not allow to achieve a high degree of fixation of the active dye and, accordingly, bright, saturated colors of textile materials. This is due to the ability of these thickeners to enter into chemical interaction with the dye is reduced due to the screening effect of the hydrocarbon radical of the chemical modifier. In addition, by increasing the thickening capacity, 2 times less thickener is applied to the fabric, and, consequently, a smaller amount of dye during washing.

Thus, as can be seen from the data in the table, the replacement of traditional thickeners with starch chemically modified with phosphate compounds leads to a significant increase in the degree of dye fixation, an increase in color intensity, a decrease in the rigidity of the printed material, and an improvement in the strength characteristics of patterned colors of textile materials.

Based on the studies carried out, we can recommend the chemically modified thickeners developed by us for industrial use in the processes of printing textile materials.

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