

celerates binding of the oxygen which is present in the viscose and in the surrounding air and, by reacting with the  $\text{Na}_2\text{S}_2$  and the  $\text{Na}_2\text{CS}_4$ , is converted into thiosulfate, and, on decomposition of the viscose in the acid precipitation bath, into elemental sulfur. Moreover, sulfur is formed in large amounts by reaction (11).

#### CONCLUSIONS

A difference in the effect of sodium sulfite additions in a model solution of caustic soda and carbon disulfide and in viscose has been shown in the process of formation of by-product sulfur-containing compounds.

Simultaneously with a retardation of ripening and an increase in homogeneity, the introduction of sodium sulfite into viscose leads to an increase in the elemental sulfur content of the yarn.

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#### REMOVAL OF HEMICELLULOSE DURING THE MERCERIZATION PROCESS

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It is well known that the low-molecular-weight fractions of cellulose and its associates (xylan and mannan), the so-called hemicellulose, adversely affect the technological process of preparing viscose, spinning fibre, and fibre physicomechanical properties. In the mercerization of cellulose, an increase in the hemicellulose content of the working alkali up to 30 g/liter causes a 1.5-fold increase in viscosity of the alkali [1], which leads to difficulties in the squeeze-out process and a decrease in the productivity of the continuous mercerization units by 10-20%. In the xanthation process, excess carbon disulfide is used up in reaction with the hemicellulose, and an increased hemicellulose content causes an impairment in the filtration process [2]. In contemporary closed water-circulating spinning cycles, plasticizing treatment, and fibre finishing, the low-molecular-weight fractions accumulate in the precipitation bath up to a concentration of 6-8 g/liter, causing clogging of the spinnerets and pipelines, and stoppage of the quartz filters.

Part of the hemicellulose (70-80% by wt.) and of the  $\beta$ -cellulose [2] goes into the fibre. Since  $\beta$ -cellulose has a low degree of polymerization (DP) (from 150 to 200), in essence it is an inert filler and it reduces the fibre strength by 1.5-2.0 cN/tex [3].

In connection with the foregoing material, an investigation of the process of removing hemicellulose during mercerization is urgent, especially if one considers that previous work was done on mercerization presses, where the cellulose is treated in the form of stacks (sheets). In mercerization in presses, diffusion equilibrium is not reached, even after treatment for 2 h, as is indicated by the large difference in hemicellulose content of the overflow and press-out alkalis. In mercerization in bulk, diffusion is practically completed after 10-15 min, as is confirmed by the establishment of a constant hemicellulose concentration in the solution (Fig. 1).

The data obtained permit one to estimate the diffusion coefficient of hemicellulose in the alkali. The diffusion coefficient will be an averaged one, since hemicellulose is a

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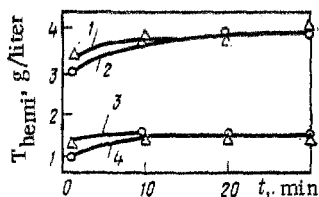


Fig. 1. Dependence of wash-out of hemicellulose in mercerization in bulk on the duration of the process (mercerization ratio = 15): 1, 2) sulfite spruce cellulose, press factors 2.8 and 3.8, respectively; 3, 4) sulfate prehydrolyzed cellulose, press factors 2.8 and 3.8, respectively.

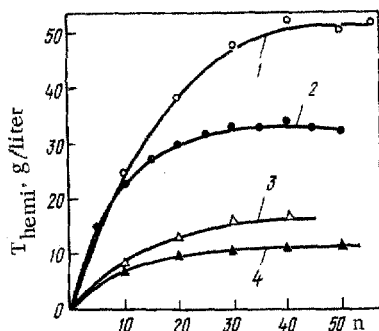


Fig. 2. Accumulation of hemicellulose in pressed-out alkali when it is used repeatedly for mercerization in bulk: 1) sulfate spruce cellulose, press factors 2.8 and 3.8, respectively; 3, 4) sulfate prehydrolyzed cellulose, cold refined, press factor 2.8 and 3.8, respectively; n is number of mercerization cycles.

polydisperse product which contains many fractions with various DP's. Nevertheless, this approximate coefficient will make it possible to compare the processes of washing out hemicellulose in mercerization in bulk and in sheets, and to draw conclusions about the mechanism by which they occur (molecular or convective diffusion).

In the mercerization of the cellulose, energetic agitation was carried out. Because of this, it may be assumed that the content of the dissolvable substance on the surface of the cellulose fibres was maintained equal to its content in the entire volume of the external alkali. Under such conditions, the Wilson formula is applicable for calculating the diffusion coefficient

$$C_t/C_\infty = 1 - R^2/4Dt \quad (1)$$

where  $C_t$  and  $C_\infty$  are the concentrations of hemicellulose at the time  $t$  and after completion of the process;  $R$  is the radius of the fibre, equal to 0.003 cm; and  $D$  is the diffusion coefficient.

As is evident from Fig. 1, after 10 min the degree of completion of the process, expressed via the ratio  $C_t/C_\infty$ , becomes equal to 0.9. In this case the expression for calculating  $D$  (in  $\text{cm}^2/\text{sec}$ ) will take the form

$$D = R^2/0.4t = 3.75 \cdot 10^{-8} \quad (2)$$

Considering the low diffusion coefficient and the squared dependence of diffusion time on linear dimensions, one can understand why an equilibrium state is not reached in merceriza-

TABLE 1. Effect of  $\alpha$ -Cellulose Content of Starting and of Alkali Cellulose on the Equilibrium Concentration of Hemicellulose in the Working Alkali

Type of cellulose	$\alpha$ -Cellulose content, % by wt.		Equilibrium concentration of hemicellulose, g/liter	
	in air-dry cellulose	in alkali cellulose	obtained experimentally	calculated by formula of [4]
Sulfite	91,5	31,5	51,0	51,2
Cold refined sulfate	91,5	23,5	33,0	34,2
	96,9	31,5	16,5	17,6
	96,9	23,5	11,5	11,8

tion in presses. In conformity with Eq. (1), for a swollen sheet of 3 mm in thickness, at a degree of process completion of 0.9, a time not less than  $(\delta/2)/0.4D$ , or 415 h, is required.

It may be assumed that in the equilibrium state the dissolved hemicellulose is uniformly distributed both in the external alkali and also in the solution present inside the cellulose fibres. In production, the working alkali solution is used repeatedly. The hemicellulose content gradually increases in it, up to some equilibrium value, depending on the hemicellulose content of the starting cellulose, the press factor, and the volume of alkali squeezed out which is withdrawn from the mercerization cycle for dialysis, dissolving, and so on.

If the squeezed-out alkali is not drawn off from the mercerization cycle, the equilibrium hemicellulose content is reached when the amount of hemicellulose coming in with the cellulose for mercerization becomes equal to the amount of hemicellulose carried out with the alkali cellulose. Since the concentration of hemicellulose in the squeezed-out alkali is equal to the concentration of hemicellulose in the alkali contained in the alkali cellulose, the equilibrium concentration of the hemicellulose can be expressed by the equation

$$C_{eq} = T_{hemi} / V_{alk} \quad (3)$$

where  $C_{eq}$  is the equilibrium hemicellulose concentration, in g/liter;  $T_{hemi}$  is the hemicellulose content of the alkali cellulose, in g/liter; and  $V_{alk}$  is the volume of alkali solution contained in the alkali cellulose, in liters.

Expressing  $T_{hemi}$  via the  $\alpha$ -cellulose content of the cellulose and the density of the alkali solution, we obtain

$$C_{eq} = \frac{\rho \alpha_{\alpha} (100 - C_{\alpha}) 1000}{C_{\alpha} (100 - A_{\alpha})} \quad (4)$$

where  $\rho$  is the density of the squeezed-out alkali, in g/ml; and  $A_{\alpha}$  and  $C_{\alpha}$  are the  $\alpha$ -cellulose contents in the alkali cellulose and in the air-dry cellulose, respectively, in % by wt.

Equation (4) was checked by attainment of the equilibrium concentration by repeated use of the working alkali solution, having a concentration of 235 g/liter, for mercerization (up to 55 mercerization cycles). After each mercerization cycle, the alkali was fortified. Hemicellulose content was determined by the procedure suggested in [2].

We used sulfite spruce cellulose and cold-refined sulfate cellulose having  $\alpha$ -cellulose contents of 91.5 and 96.5% by wt., respectively. Pressing out was carried out to an  $\alpha$ -cellulose content in the alkali cellulose of 31.5 and 23.5% by wt., that is, to a press factor of 2.8 or 3.8.

The results obtained are presented in Fig. 2. The equilibrium concentration for a sulfite cellulose containing 91.5% by wt.  $\alpha$ -cellulose is reached after 50-55 cycles and is 51 g/liter for a press factor of 2.8 and 33 g/liter for a press factor of 3.8.

As is evident from Table 1, the equilibrium concentration calculated by Eq. (4) differs slightly from the experimental value. Hence it follows that the total hemicellulose content in alkali cellulose in mercerization in bulk depends only on the hemicellulose content of the

starting cellulose and the amount of alkali squeezed out which is withdrawn from the mercerization cycle (for dialysis, dissolving, for sewerage, etc.) and does not depend on the  $\alpha$ -cellulose content of the alkali cellulose.

### CONCLUSIONS

The hemicellulose content of the squeezed-out alkali and of the working alkali depends only on the hemicellulose content of the starting cellulose, on the  $\alpha$ -cellulose content of the alkali cellulose, and on the amount of the squeezed-out alkali which is drawn off from the mercerization cycle.

The total hemicellulose content of the alkali cellulose in mercerization in bulk does not depend on the  $\alpha$ -cellulose content of the alkali cellulose.

The use of an alkali cellulose containing 23-24%  $\alpha$ -cellulose will make it possible to reduce the hemicellulose content of the working and squeezed-out alkali by 16-18 g/liter.

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### PRECIPITATING POWER OF AQUEOUS SOLUTIONS IN SPINNING

#### CUPRAMMONIUM FIBRES

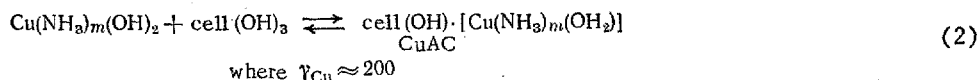
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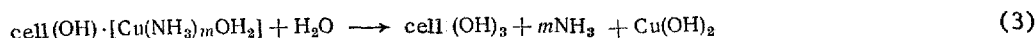
The preparation of hydrocellulose fibres by the viscose method is fraught with difficulties due to the need to protect the environment from contamination. Therefore attention has been drawn again to the manufacture of fibres from cuprammonium cellulose spinning solutions. This manufacturing process is practically harmless if the regeneration of copper and ammonia is properly organized, and can ensure production of textile fibres and yarns with the same physicochemical properties as viscose fibres and yarns if the freshly-spun fibres are subjected to orientation stretching.

At present four fundamental methods of spinning fibres from cuprammonium cellulose spinning solutions are known: the aqueous one, the alkaline one [1], the acidic one (into sulfuric, nitric, or phosphoric acid precipitation baths) [2-4], and the aqueous-organic (solutions of organic compounds which mix with water).

Regardless of the spinning method, the cellulose solution process can be described by the following equations:



Decomposition of the CuAC (cuprammonium cellulose complex) at various precipitation bath compositions takes place by the following equations:




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