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DEPENDENCE OF THE SUPERMOLECULAR STRUCTURE OF COTTONPLANT STEM CELLULOSE ON THE TECHNOLOGICAL PROCESSES OF ITS PRODUCTION

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Electron microscopy, IR spectroscopy, and x-radiography have been used to study the supermolecular structure of guza-paya cellulose obtained by the following technological methods: alkaline cook, bleaching with hydrogen peroxide, and acidification; alkaline cook in the presence of anthraquinone, oxygen-soda cook, bleaching and acidification; and alkaline cook in the presence of anthraquinone and hexamethylenetetramine, followed by an oxygen-soda cook, bleaching, and acidification. It has been shown that the structure of the cellulose depends on the method of its production, but changes take place only at the supermolecular level, without affecting the fine structure.

The intensive development of the chemical, pulp and paper, and hydrolysis industries is responsible for the necessity of broadening the raw materials basis for cellulose through the use of cellulose-containing materials from annual plants. In forest-free regions, such as Central Asia, an important cellulose-containing raw material consists of cottonplant stems — guza-paya. The question of the use of guza-paya is not new [1-4] but this material has not so far found wide use.

Some properties of cellulose isolated from guza-paya have been investigated and its suitability for the production of paper and cardboard and even artificial silk has been shown [5-7]. The authors concerned carried out cooks of guza-paya by the sulfate, sulfide, soda, and nitric acid methods. A comparatively new and ecologically friendly method of obtaining cellulose from low-quality cotton lint and guza-paya is the oxygen-soda cook [8, 9].

We give the results of an investigation of the structural changes of cellulose taking place during the following technological processes for obtaining it from guza-paya: alkaline cook, bleaching with hydrogen peroxide, and acidification; alkaline cook with the addition of anthraquinone, oxygen-soda cook, bleaching with hydrogen peroxide, and acidification; alkaline cook with the addition of anthraquinone and hexamethylenetetramine, oxygen-soda cook, bleaching with hydrogen peroxide, and acidification. To evaluate the structural changes we used electron microscopy, IR spectroscopy, and x-radiography.

The results of the electron-microscope investigations of the cellulose samples show that the surface of the initial guza-paya fibers was characterized by the presence of shallow wrinkles filled with noncellulosic substances (Fig. 1*a*). After an alkaline cook, bleaching, and acidification of the guza-paya, because of the elimination of the noncellulosic substances the wrinkled structure of the cellulosic fiber was obvious (Fig. 1*b*).

The addition of anthraquinone during an alkaline cook led to a swelling of the surface of the cellulose and the structure of the primary wall of the fiber was not revealed, but after an oxygen-soda cook, bleaching, and acidification the noncellulosic components were removed from the surface of the fiber to a considerable degree, and, in places, the individual fibrils of the primary wall were clearly revealed (Fig. 1*c*).

An alkaline cook of the guza-paya with the addition of anthraquinone and hexamethylenetetramine purified the cellulose still more, and the surface of the fiber acquired a distinct wrinkled structure. The wrinkles were arranged at an acute angle to the axis of the fiber. In the subsequent processes of an oxygen-soda cook, bleaching, and acidification, the cellulose fiber swelled greatly, the wrinkles in its surface were smoothed out, and the reticular fibrillar structure of the primary wall was clearly revealed (Fig. 1*d*).

Characteristic changes of the internal structure can be observed in an investigation of fragments of the secondary wall of the samples mentioned. When the initial sample of guza-paya was subjected to mechanical and ultrasonic dispersion, a fairly

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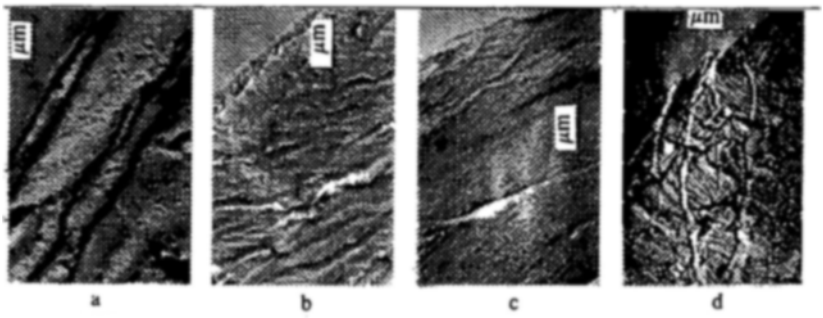

Fig. 1. Electron photomicrographs of replicas from the surface of the initial guza-paya (*a*) and of the cellulose obtained from it by an alkaline cook, bleaching, and acidification (*b*); by an alkaline cook in the presence of anthraquinone, an oxygen-soda cook, bleaching, and acidification (*c*); by an alkaline cook in the presence of anthraquinone and hexamethylenetetramine, an oxygen-soda cook, bleaching, and acidification (*d*).

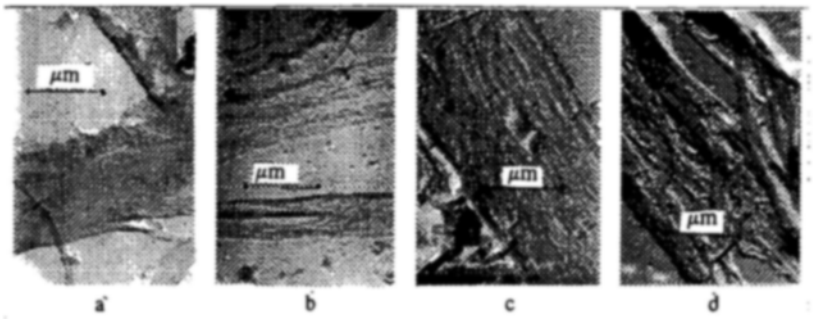

Fig. 2. Electron photomicrographs of fragments of the internal fibrillar structure of a guza-paya fiber (*a*) and of the cellulose obtained from it by an alkaline cook with the addition of anthraquinone and hexamethylenetetramine, an oxygen-soda cook, bleaching with hydrogen peroxide, and acidification.

dense layer was formed in which the fibrillar aggregates appeared to be strongly agglutinated by noncellulosic substances (Fig. 2*a*). After the alkaline cook, bleaching, and acidification, the lignin and other fatty-waxy substances had been eliminated and, with fragmentation of the internal structure, dense-packed fibrils of the secondary wall of the cellulose fiber were detected (Fig. 2*b*).

The addition of anthraquinone during an alkaline cook led to still greater elimination of the noncellulosic impurities, and, as a result, fragments with a distinct fibrillar structure appeared. The subsequent processes of an oxygen-soda cook, bleaching, and acidification led to some ordering of the dense packing of the fibrillar aggregates of the cellulose (Fig. 2*c*).

In the case of an alkaline cook of guza-paya with the addition of anthraquinone and hexamethylenetetramine, followed by an oxygen-soda cook, bleaching, and acidification, the inner layer of the cellulose fiber swelled greatly, and the fibrils became more disoriented (Fig. 2*d*).

Changes in the fine structure of the cellulose were studied on crystallites of the corresponding samples of cellulose obtained by heterogeneous acid hydrolysis — by boiling in 2.5 N H_2SO_4. In addition to crystallites, this formed long and thin microfibrils and also spherical particles with different dimensions that were products of the decomposition of the noncellulosic impurities (Fig. 3*a*). The formation of fairly long microfibrils was due to the fact that part of the sulfuric acid was consumed in the breakdown of the noncellulosic impurities. After the alkaline cook, hydrolysis broke down the cellulose into crystals of different lengths (Fig. 3*b*). The addition of amino-containing stabilizers and also the subsequent processes of an oxygen-soda cook and bleaching had no appreciable influence on the form and dimensions of the crystallites (Fig. 3*c**). IR-spectroscopic and x-radiographic investigations completely confirmed the electron-microscope results.

*Sic. Figure 3*c* is not shown – Translator.

TABLE 1. Changes in the Area of the Absorption Band of Hydroxy Groups Involved in Hydrogen Bonds (S_{OH}) and in the Degree of Crystallinity (DC) with Various Methods of Obtaining Cellulose from Guza-Paya

Characteristics of the sample	S_{OH}, cm^2	DC %
Initial guza-paya	80	26.0
Alkaline cook, bleaching with hydrogen peroxide, and acidification	103	50
Alkaline cook with the addition of anthraquinone, oxygen-soda cook, bleaching with hydrogen proxide, and acidification	107	60
Alkaline cook with the addition of anthraquinone and hexamethylenetetramine, oxygen-soda cook, hydrogen peroxide bleaching, and acidification	121	64.0

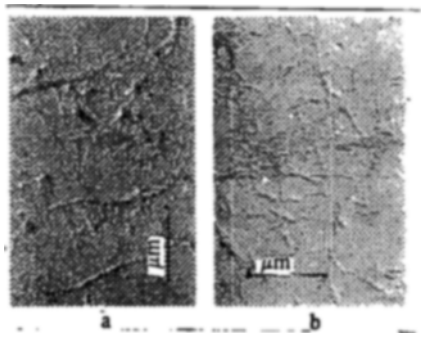

Fig. 3. Electron photomicrograph of crystallites of microfibrils of cellulose in the initial guza-paya and after its refining by an alkaline cook, bleaching, and acidification.

An increase in the area of the absorption band of hydroxy groups involved in hydrogen bonds in the guza-paya cellulose after cooking and bleaching (Table 1) can be explained by the considerable degree of elimination of lignin and other noncellulosic impurities between the layers of cellulose microfibrils, as a result of which OH groups were freed and the packing of the microfibrils into layers became more ordered.

After the oxygen-soda cook and bleaching, the value of S_{OH} had decreased, i.e., there was a loosening of the supermolecular structure of the cellulose, as was confirmed by electron-microscope investigations. The comparatively low degree of crystallinity (DC) of the initial guza-paya is explained by the presence in it of more than 60% of noncellulosic components with an amorphous structure. As a result of the various refinement processes, the cellulose content of the samples increased and the DC rose. The bleaching processes led to a still greater elimination of noncellulose substances and, correspondingly, to a further rise in the DC.

EXPERIMENTAL

For the electron-microscope investigations we used a TESLA-BC242E electron microscope, with observation at direct electron-optic magnifications of up to 10,000. The methods of preparation involved the two-stage production of polystyrene–carbon replicas from the surfaces of the samples, and mechanical dispersion and acid hydrolysis in combination with ultrasonic action. This method is described in more detail in [10].

The x-radiographic investigations were conducted on a URS-50 HM apparatus. Samples were prepared by the following procedure: finely comminuted fibers were passed through a sieve, and tablets were formed in a special mold under a pressure of 5 t/cm^2; x-radiograms were taken of these using monochromatized CuK_α radiation. The degrees of crystallinity were calculated from the x-radiographic results by means of the formula proposed in [11].

The IR-spectroscopic investigation was made on a UR-10 spectrophotometer by the procedure described in [12].

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