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Labile products of interaction of cellulose with nitrogen oxide compounds

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Abstract. Data concerning the conditions and kinetics of the formation, the methods for identification and isolation, the chemical and physical properties, and the crystal structure of cellulose trinitrite are presented. The conditions governing the formation of Knecht' sorption compound and other unstable crystalline products in the cellulose – N_2O_4 system are also discussed. The primary role of labile derivatives in the manifestation of polymorphism by cellulose on its regeneration from these compounds is demonstrated. The causes of the amorphisation of cellulose,which may occur in these systems, are examined. Examples of a rational combination of several functions of the reaction medium and of the labile nitrogen-containing compound present in it in the preparation of other materials of practical importance from polysaccharides (sulfate and acetate esters and structurally and chemically modified powdered forms of cellulose) are presented. The bibliography includes 160 references.

I. Introduction

The possibilities for the chemical and physical transformation of cellulose (Cel) with the aid of nitrogen oxide compounds (N_2O_4, NO_2, N_2O_3, HNO_3) are extremely diverse. The use of these compounds in oxidation,[1,2] nitration,[3,4] degradation,[5,6] bleaching,[7,8] and structural modification [9–12] of cellulose, the dissolution of cellulose in aprotic electron-donating organic media,[13–15] and its conversion into various derivatives,[16–18] fibres,[13,19–21] membranes,[22–24] and composite materials [20,25] is well known. In terms of the 'universality index', nitrogen oxide compounds (in the first place N_2O_4) are superior to all known reagents which actively interact with cellulose. The nature of the transformations of cellulose on treatment with these compounds depends on the reaction conditions.

The postulated formation in the given systems of labile cellulose derivatives and their influence on the course of the transformations and the properties of the final products have long been the subject of controversy. A key chemical compound of this type is cellulose nitrite. The decrease in the stability of pyroxylin has been attributed to its presence.[3,26] The familiar mechanism [28] of the oxidation of cellulose to monocarboxycellulose, where the role of an intermediate was assigned to cellulose nitrite, has been supported [2] and rejected.[1,27] The dissolution of cellulose in aprotic organic media containing N_2O_4 is to this day explained in different ways. Some investigators [13,16—18] postulate the formation of cellulose nitrite whilst others [15] believe that molecular complexes are formed. The absence of information about cellulose nitrite as an individual compound as well as the lack of reliable methods for its detection in a complex reaction medium gave to this cellulose derivative the attributes of a 'hypothetical compound' until recently.

An unstable sorption product characteristic of the given systems is the adduct of cellulose with HNO_3, the existence of which was established at the beginning of this century by Knecht [29] and was subsequently called Knecht's compound (KC).[30,31] It has been suggested that the formation of KC precedes the nitration of cellulose.[3] For many decades KC remained 'in the shade' and neither its chemical composition and structure nor its crystal structure have been established hitherto. Nevertheless, communications have recently appeared,[32,34] indicating the possibility of an effective practical application of KC.

Cellulose nitrite and molecular complexes as possible alternatives to the latter have been considered in reviews [13–15] merely in the context of their probable participation in the dissolution of cellulose. Their formation was postulated on the basis of a series of indirect experimental pieces of evidence. It was not until the 1980s that the labile products of the interaction of cellulose with N_2O_4 became the object of special comprehensive investigations and fairly extensive experimental data have now accumulated in this field. The high degree of stoichiometry of the interaction observed in this system has led to the possibility of the effective employment of X-ray diffraction for the detection of cellulose nitrite, KC, and other unstable compounds in terms of their crystalline phases in a complex reaction mixture. The primary role of labile derivatives of cellulose also in the observed diversity of the heterophase structural transformations of cellulose, which do not lead ultimately to an alteration of its chemical composition, has been elucidated. The application of new methods made it possible to overcome the 'inaccessibility' of cellulose trinitrite.

Data concerning the conditions and kinetics of the formation, the methods for the identification and isolation, the crystal structure, the properties, and the applied importance of labile nitrogen-containing derivatives of cellulose compounds should be of interest to a wide range of specialists in the field of the chemistry and physics of cellulose. The present review is the first attempt at a systematic account and survey of this scattered information.

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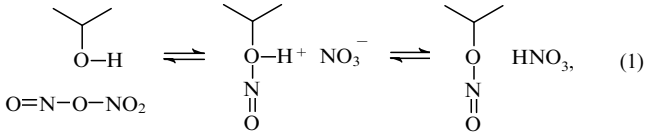
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II. Analysis of ideas concerning the preparation and isolation of cellulose nitrite

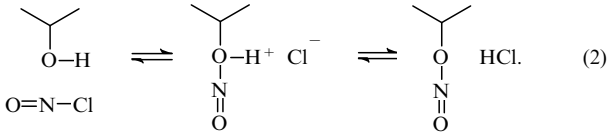
The first mention of cellulose nitrite is in the communication of Nicolardot and Chertier.[35] Its authors detected nitrite ester groups in the product of the interaction of cellulose with a mixture of nitrogen oxides and acetic acid (AA). The formation of cellulose nitrite was postulated in the nitration of cellulose by compositions containing nitrogen oxides in connection with the search for ways of increasing the stability of nitrocellulose.[26]

Studies on the formation reaction of monocarboxycellulose have shown that the UV and visible spectra of cellulose treated with gaseous nitrogen oxides exhibit a series of absorption bands at 350, 341.5, 355, and 365 nm, which may be due either to HNO_2 or to cellulose nitrite. A detailed experimental test of both possibilities indicated that these bands are due to the cellulose nitrite spectrum.[28] A mechanism postulating that the oxidation of cellulose by nitrogen oxides proceeds via the formation of cellulose nitrite as an intermediate has been put forward.

The practical importance of cellulose nitrite was revealed by numerous studies [13–18, 36–53] concerning the use of nitrosyl-containing compounds — N_2O_4, NOCl, $NO[SO_4H]$, etc. — in combination with aprotic organic solvents for the dissolution of cellulose. Fowler et al.[36] observed that in nonpolar solvents N_2O_4 has a strong oxidising effect on cellulose, whereas in polar solvents increased swelling takes place or the polymer dissolves without appreciable oxidation. The most suitable organic components from the standpoint of the preparation and processing of the solutions proved to be dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dimethylacetamide (DMA), and ethyl acetate (EA).[15, 27] The formation of the nitrosyl nitrate form of N_2O_4 ($NO^+NO_3^-$) in polar solvents in the presence of this isomer even in HNO_3-free liquid N_2O_4 has been demonstrated [54–56] the interaction of the strong electron acceptor NO^+ with the oxygen atom of the hydroxy-group of cellulose, which functions as an electron donor, is typical for these systems.[16, 42, 44, 46] Such interaction leads to the formation of cellulose nitrite and HNO_3, which dissolve in the reaction medium. The organic solvent binds HNO_3, displacing thereby the equilibrium towards the formation of cellulose nitrite. Total dissolution is ensured for the molar ratio N_2O_4 : Cel = 3. When NOCl is combined with DMF, the ratio is 8.[13, 16] In contrast to N_2O_4, nitrosyl chloride itself interacts chemically with DMF.[15] The following mechanism of the electrophilic substitution involving all the hydroxy-groups of cellulose has been proposed:[16]



(1)



(2)

This view is also adhered to by Ermolenko,[28] who postulated the formation of cellulose nitrite from its adsorption compound with the nitrosyl nitrate form of N_2O_4.

The high sensitivity of solutions of cellulose nitrite in nitrosating compositions to water and alcohols has been noted.[38, 39, 44–47] The regeneration of cellulose is catalyzed by the acid present in the system, which corresponds to the inversion of reactions (1) and (2). The chemical composition of the substance isolated on hydrolysis or alcoholysis hardly differs from that of the initial cellulose.[13, 16, 44, 46] The acid present in the solution induces the depolymerisation of the macromolecules when the solution is maintained at room temperature.[16] Allowing the solutions to stand in the cold (5 °C) for between 6 h and 12 days does not reduce appreciably the degree of polymerisation (DP) of the cellulose regenerated from them. Depolymerisation occurs also during the nitrosation process.[52, 53] The degree of depolymerisation depends greatly on the moisture content of cellulose stirring of the solutions promotes depolymerisation.[52]

The possibility of synthesising in solution other uniformly substituted cellulose derivatives has been attributed to the formation of cellulose nitrite and to its reactivity in transesterification reactions.[16–18, 41 43, 50] The water-soluble cellulose nitrate has been obtained by Schweiger [16] as a result of heating a solution of cellulose nitrite in the N_2O_4–DMF mixture for 70 min at 90 °C. Its degree of substitution (DS) was only 0.5. The HNO_3 accumulated in the system as a result of the nitrosation of cellulose proved to be sufficient for the reaction to occur. These results explained the observations of Clermont and coworkers,[41–43] who carried out similar experiments and who postulated that the weakly substituted highly degraded product formed is a mixed cellulose nitrite–nitrate. At room temperature, cellulose is not nitrated in the given system. Even after the solution has been kept together with added HNO_3 for 20 h (molar ratio HNO_3 : Cel = 9), only traces of nitro-groups are detected in the precipitated product (DS = 0.04).[47]

Low-molecular-mass alkyl nitrites, including those obtained by treating monohydroxylic alcohols with N_2O_4, can be isolated after diluting the reaction medium with water, in which they are insoluble.[44, 57] Polyol nitrites are much less stable than the nitrites of monohydroxylic alcohols,[58] which can be accounted for by the anchimeric facilitation of the hydrolytic reaction by the vicinal nitrite ester groups. For example, the nitrites of poly(vinyl alcohol) and glycerol cannot be isolated on dilution with water owing to their low hydrolytic stability in acid media. The stability of cellulose nitrite is even lower because of the extensive capillary-porous system of the fibre, which increases the area of the reactive surface. Schweiger [16, 44] precipitated cellulose nitrite with ice water from a solution to which a strong organic base (pyridine, quinoline, or triethylamine) had been added. The role of the base consisted in inhibiting the acid catalysis of the elimination of the nitrite ester groups. The white deposit isolated was washed with ice water, hydrolysed in an acid medium, and the HNO_2 content in the liquid over the precipitated polymer was determined. The moist cellulose nitrite thus obtained may be stored for a long time in the cold without decomposition. All attempts to dry it led to decomposition. Wagenknecht and coworkers [46, 48] precipitated and analysed cellulose nitrite in accordance with the same scheme, employing a mixture of diethyl ether (DE) and methylene chloride as the precipitant. The nitrogen content in the precipitates corresponded to a degree of substitution of 2.50–2.95 in terms of the nitrite ester groups,[46] which, together with the ease of their hydrolysis or alcoholysis, indicated the occurrence of *O*-nitrosation.

The product isolated by Schweiger [16, 44] was identified more rigorously by Torgashov et al.[59] Analysis of the deposit for nitrogen in the nitrate and nitrite forms demonstrated that the latter predominated greatly (2.85 against 0.01 in terms of the degree of substitution). For the first time, the IR and UV spectra of a preparation of an individual highly substituted cellulose nitrite were presented. The nitrite was prepared by the following method. The fibrous deposit from which excess water had been squeezed out was dissolved in ethyl acetate cooled to 5 °C. Water was removed from the resulting solution by successive freezing and treatment with calcium chloride. Specimen films for spectroscopic study were cast on KRS-5 or quartz plates in a vacuum desiccator over P_2O_5. The IR spectrum of such a film (Fig. 1) hardly exhibits the band due to the stretching vibrations of the cellulose OH groups (3100–3500 m^{-1}) as a consequence of the high degree of substitution, which is 2.85. The two new intense bands at 780 and 1680 cm^{-1} correspond to the stretching vibrations of the O–N and N=O bonds in organic nitrites.[60] The low-intensity bands at 510 and 650 cm^{-1} may be assigned to the deformation vibrations of the O=N–O group.

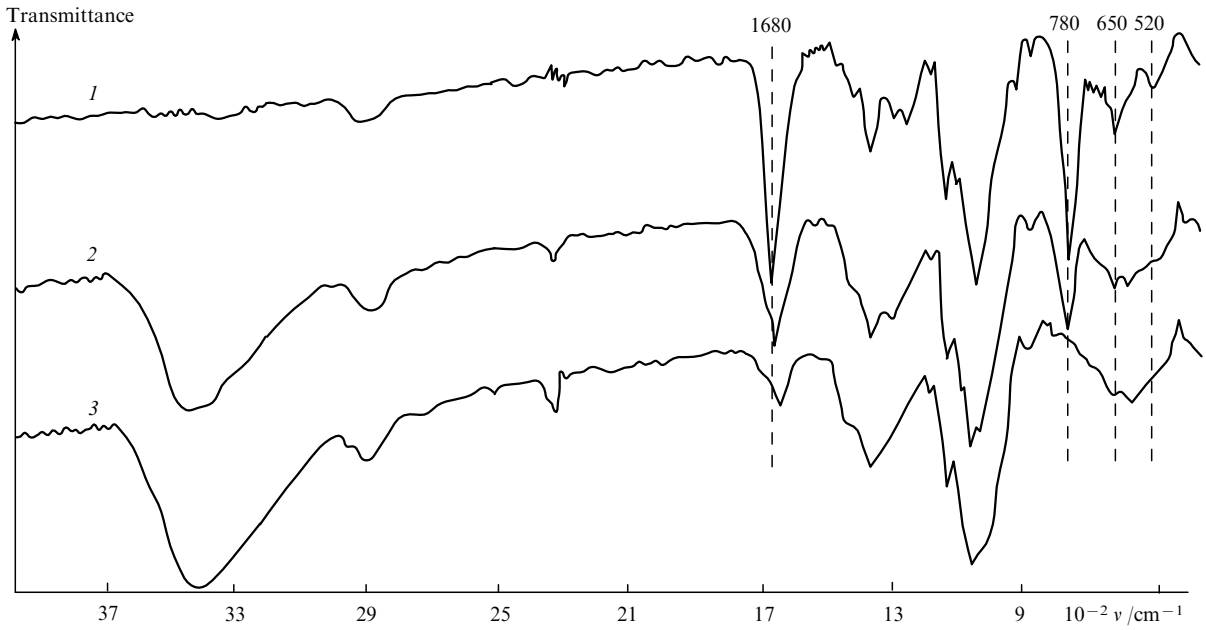


Figure 1. IR spectra of the initial cellulose nitrite film (*1*) after keeping in air for 30 min (*2*), and after 2 min contact with ethanol (*3*).

An obligatory condition for the measurement of such a spectrum is the reduction to a minimum of the contact between the specimen and the moisture in the ambient medium during all the preparatory operations. In air with a relative humidity of 65%–70%, at 20 °C, the preparation decomposes, which has been clearly detected from the increase in the intensity of the absorption in the region of the stretching vibrations of the cellulose OH groups and the synchronous weakening of the spectral bands due to the nitrite ester. The weakening of the band at 1680 cm^{-1} is accompanied by its bathochromic shift. The spectrum recorded after brief treatment of the film with water or ethanol corresponds to chemically unaltered cellulose.

The results of the spectroscopic experiments have been confirmed by Grinshpan,[15] who, whilst retaining Schweiger's method,[16] precipitated cellulose nitrite from the N_2O_4–acetonitrile system. According to these data, the 1660 and 1780 cm^{-1} bands were present in the IR spectrum of a film of the highly substituted product (DS = 2.80) and an appreciable absorption was noted in the range 3100–3500 cm^{-1}. The appearance of the latter as well as the displacement of the N=O bond stretching vibration band maximum from 1680 to 1660 cm^{-1} are most probably caused by the partial decomposition of the specimen during the experiments. Thus the presence of absorption bands at 1780 cm^{-1} and in the range 1650–1680 cm^{-1} must be regarded as specific characteristic of the IR spectrum of cellulose nitrite. This characteristic is common to all nitrite esters.[57, 60]

The formation of cellulose nitrite in the above systems, and not of its complexes with nitrogen oxides,[15, 27, 36, 61] has been confirmed also by the results of the analysis of the solutions for HNO_3, the second product of the esterification reaction. The amount of HNO_3 was determined from the mass of the pyridinium nitrate precipitated when an excess of pyridine was added to a solution of cellulose in the N_2O_4–ethyl acetate mixture. Absolute diethyl ether, which is incapable of precipitating the polymer, was used in addition to isolate pyridinium nitrate from the N_2O_4–DMF system. According to the experimental data approximately 3 moles of HNO_3 per glucopyranose unit (GPU) of cellulose are present in the solutions, i.e. as much as should have been obtained on total esterification of cellulose.

It has been suggested [14] that the presence of a strong organic base is obligatory for the *O*-nitrosation of cellulose, because cellulose nitrite can be isolated from solution only with participation of amines.[16, 44, 46, 48] Developing further this hypothesis, Grinshpan [15] attributes to amines the role of a catalyst in the esterification of cellulose by the nitrous acid formed when the nitrogen oxides of the solvent mixture interact with water in the precipitation baths. It has been suggested that, apart from the catalytic effect, the presence of amines prevents the decomposition of HNO_3. The cause of the high content of nitrite ester groups (DS = 2.50–2.95) in the deposits isolated without the use of water was not discussed in this connection.[46, 48]

The catalytic function of amines is confirmed, according to Grinshpan's data,[15] by the procedure described in a inventor's certificate.[62] According to this procedure, cellulose nitrite can be precipitated from solutions at the instant of formation by employing a cooled water–pyridine mixture. It was noted that the cellulose nitrite isolated from solutions incorporating an organic component with a lower proton affinity (ethyl acetate or acrylonitrile and not DMF or DMSO) is the most stable. This factor is assessed as an argument in support of the dissolution of cellulose without esterification to the nitrite. It has been stated that if an esterification had occurred, the product isolated from solution in DMF or DMSO would be more stable. However, it is evident that in the presence of amines, the proton affinity towards the solvent loses its importance and an effect of 'protection' of cellulose nitrite against water should be manifested in more hydrophobic media (of the type of ethyl acetate).

The possibility of the *O*-nitrosation of cellulose, even in the absence of amines on its dissolution in nitrosyl-containing systems with a 'dual' esterifying ability: NO[HSO_4]–DMF, NO[$SbCl_6$]–DMSO, has been assumed.[15] According to the author, the anionic components of the salt-like compounds in such systems perform simultaneously the functions of esterifying agents, *O*-nitrosation acid catalysts, and stabilisers of the HNO_2 and the cellulose nitrite formed.

The following reaction equations have been presented:

$$\mathrm{Cel{-}(OH)_3 + NO[HSO_4] \longrightarrow Cel\begin{matrix}(OSO_3H)_x\\(OH)_{3-x}\end{matrix} + HNO_2,} \qquad (3)$$

$$\mathrm{Cel\begin{matrix}(OSO_3H)_x\\(OH)_{3-x}\end{matrix} + HONO \rightleftharpoons Cel\begin{matrix}(OSO_3H)_x\\(ONO)_y\\(OH)_{3-x-y}\end{matrix} + H_2O,} \qquad (4)$$

$$\mathrm{NO[HSO_4] + H_2O \longrightarrow H_2SO_4 + HONO.} \qquad (5)$$

The nitrite ester groups in the mixed cellulose ester formed are fairly stable.[45,46,48] A substantial part of them (DS = 1.21) can be detected together with sulfate groups (DS = 1.19) in the deposits isolated at 20 °C by means of acetone without using amines.[45] On the other hand, the content of nitrite groups in the deposits obtained by similar procedures from the N_2O_4–DMF and NOCl–DMF solvent systems is very small, which, according to Grinshpan,[15] confirms the absence of reactions similar to reactions (3)–(5) and the constancy of the chemical composition of the cellulose dissolved in these media. However, even if the latter possess a nitrosating activity, one cannot expect a high concentration of nitrite ester groups in the products precipitated with acetone, in which the highly substituted cellulose nitrite is readily dissolved.[15,57] The ability of ketones to enolise in acid media induces denitrosation and hence the deposition of the polymer. When N_2O_4 is combined with acetone, a stable solution cannot be obtained because of enolisation.

The majority of investigators [37,40,41,44,46,51,52,63,64] attribute the dissolution of cellulose to the esterifying ability of nitrosyl-containing compounds (in the first place N_2O_4) in the absence of amines. Other views on this process have been expressed in studies [15,27,36,61] in which the postulated compositions and structures of the molecular complexes, ensuring, according to the authors, the dissolution of cellulose, are discussed. The results of the analysis of the solutions by UV,[15,57,59] IR,[15,24,59,65] ^{1}H NMR,[15,51] and ^{13}C NMR [15,49] spectroscopic methods as well as calorimetry [15,63] have been treated in a contradictory manner by the supporters and opponents of the nitrite mechanism of the dissolution of cellulose. The IR spectra of the Cel–N_2O_4–DMSO system (Fig. 2) contain evident features of the esterification of cellulose, such as the decline of the intense absorption in the range 3100–3500 cm^{-1} and the appearance of bands characteristic of the nitrite ester substituents introduced into the chain (at 1650 and 730 cm^{-1}).[24,57,65] The dissolution of the model cellulose nitrite in DMSO induces a shift of the N=O bond stretching vibration band maximum from 1680 to 1660 cm^{-1}, while the position of the band at 780 cm^{-1} is retained. A similar phenomenon has been observed also for low-molecular-mass nitrites in polar solvents.[66] The position of the absorption band of pentyl nitrite at 1650 cm^{-1} remained unchanged after dissolution in CCl_4,but was displaced to 1630 cm^{-1} after dissolution in $CHCl_3$.

Analysis of the IR spectra obtained in a number of studies [24,57,65] (Fig. 2) showed that the spectrum of the Cel–N_2O_4–DMSO system can be regarded, with some approximation, as a superposition of the spectra of solutions of cellulose nitrite and HNO_3 in DMSO. The absorption maxima of the dissolved cellulose nitrite (1660 cm^{-1}) and HNO_3 (1640 cm^{-1}) are not then resolved. For the Cel–N_2O_4–DMSO system, they are averaged out at about 1650 cm^{-1}.

The use instead of cellulose of its analogue soluble in DMSO, namely starch, makes it possible to trace the variation of the absorption under the influence of N_2O_4 in the region of the stretching vibrations of the OH groups of the polysaccharide (Fig. 3). The addition of N_2O_4 to a solution of starch (up to 3 moles per GPU) induces a pronounced weakening of the intensity of the absorption band due to the OH groups. The bathochromic shift of this band (from 3310 to 3240 cm^{-1}) taking place simultaneously with the changes in intensity can be logically explained by the different reactivity of the reaction of the OH groups, depending on the energy of the hydrogen bonds, similar to that in the synthesis of the nitrites of other polyols.[58] A number of the most strongly bound hydroxy-groups remain free. An increase in the N_2O_4 concentration in solution also leads to a steady intensification of the spectroscopic indications of the presence of starch nitrite (bands at 1650 and 780 cm^{-1} and HNO_3, (2100–2600, 1340 820, and 620 cm^{-1}). In the measurement of the IR spectra of solutions, it is necessary to take into account the high sensitivity of the preparation in the form of a thin liquid layer to atmospheric moisture. The increase in the intensity of the absorption band of the cellulose OH group is the spectroscopic evidence of the rapid decomposition of cellulose nitrite.

According to Grinshpan,[15] the IR spectra of the Cel–N_2O_4–DMSO system do not conflict with the hypothesis that cellulose dissolves via the formation of a Cel–organic solvent–NO_2 ternary complex. The reasons for the marked weakening of the absorption intensity in the range 3100–3500 cm^{-1} are not discussed. It is postulated that the bands at 1650 cm^{-1} (at 1640 cm^{-1} according to Grinshpan [15]) and 1340 cm^{-1} (Fig. 2)

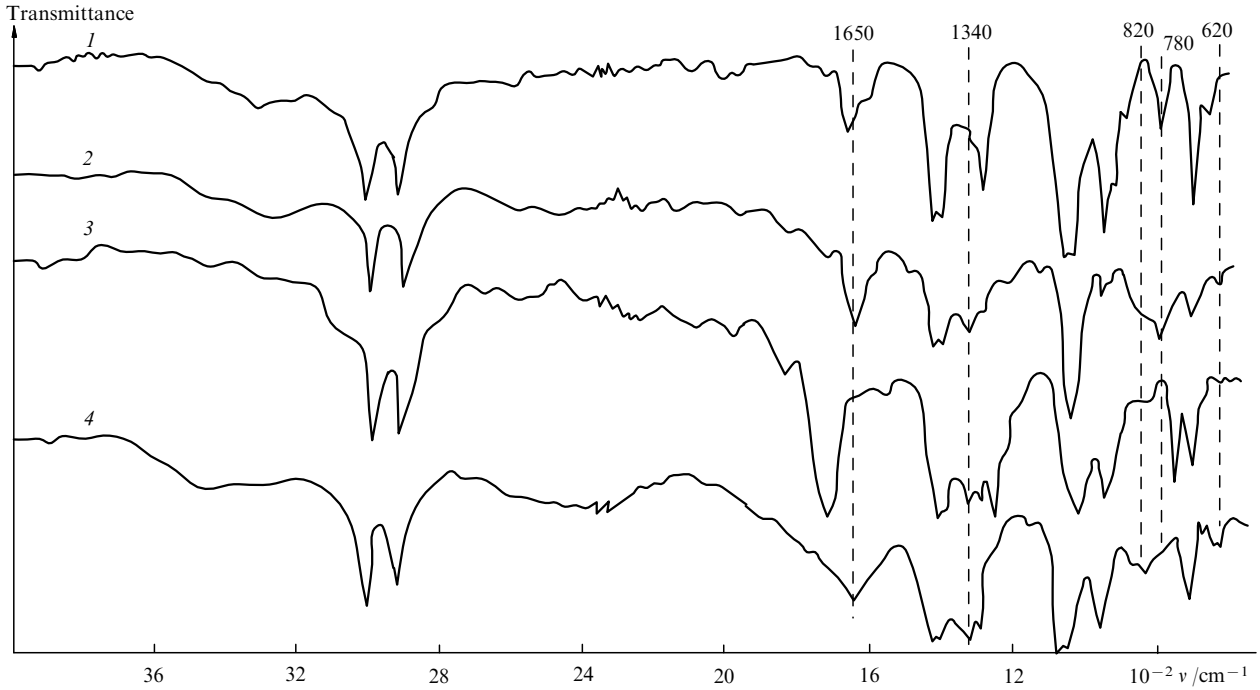


Figure 2. IR spectra of a 15% solution of cellulose nitrite (DS = 2.85) in DMSO (*1*) of the Cel–N_2O_3–DMSO (10 : 17 : 73 mass %) homogeneous system (*2*), and of the N_2O_4–DMSO dissolving mixture (*3*) and of 11.6 mass % HNO_3 solution in DMSO (*4*).

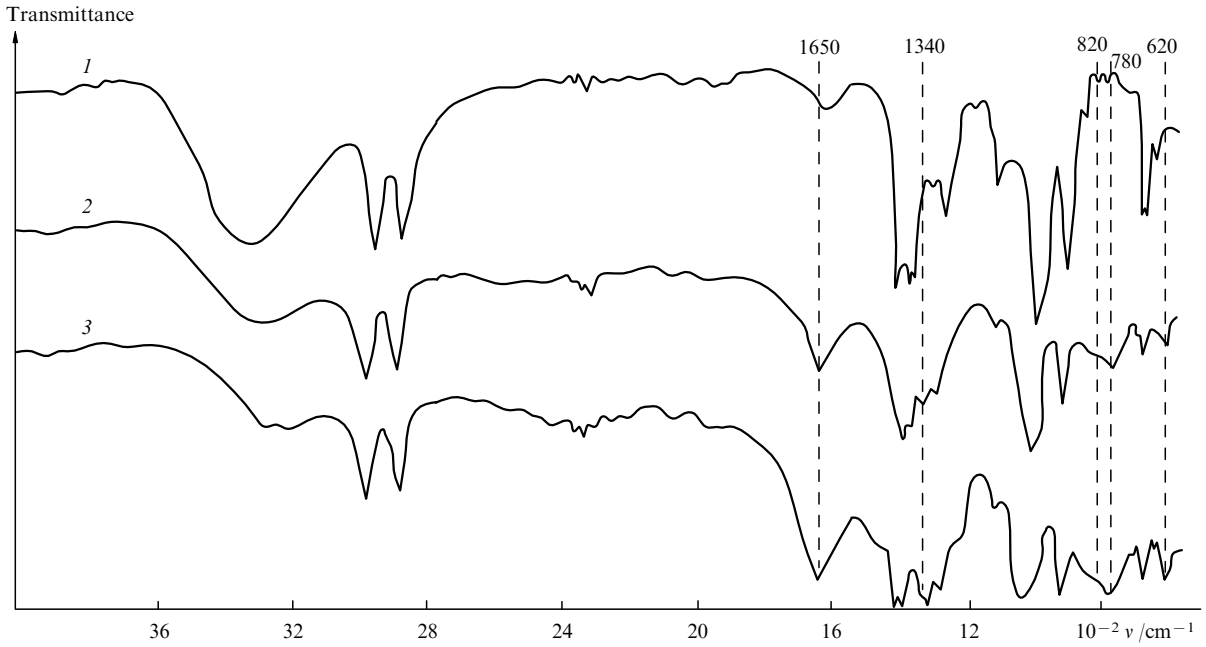


Figure 3. IR spectra of an 8% solution of starch in DMSO (*1*) and of the same solution to which two (*2*) and three (*3*) moles of N_2O_4 per GPU have been added.

are due to the NO_2 molecules bound in a complex with DMSO. This explanation is not based on any known reference guidelines similar to those in the spectra of low-molecular-mass nitrites. For systems incorporating nitrogen oxides with different degrees of oxidation and the products of their heterolytic dissociation (nitric and nitrous acids), the controversial character of such assignments of the spectral bands is evident. The explanation of the appearance of the 780 cm^{-1} band by the formation of a nonchemical sorption compound of cellulose and anhydrous HNO_2 is likewise controversial. The latter arises in the system '...on homogeneous dissociation of a C–H bond in the alcoholic groups of cellulose effected with the aid of the NO_2 radical molecules'.[15] The origin of the bands at 1420, 1300, and 940 cm^{-1} is also attributed to the formation of a stable Cel–HNO_2 sorption complex. However, the intensity of precisely these bands in the spectrum of a solution of starch in DMSO is appreciably higher than in the spectrum of the same solution containing N_2O_4 (Fig. 3). The explanation of a series of observations in Grinshpan's study,[15] which follows from the known similarity of certain spectral features of HNO_2 and organic nitrites, repeats essentially the hypothesis previously tested by Ermolenko [28] and rejected.

Philipp and coworkers,[17, 45–50] who have investigated extensively the state of cellulose in nitrosyl-containing solvent systems, allow (in the papers by Nehls et al.[49] and Philipp et al.[50]) the possibility of equilibrium between the cellulose nitrite ester and its adduct with N_2O_4 via a subsidiary valence. This conclusion was based on the analysis of 13C NMR spectra of the Cel–N_2O_4–DMF system,[49] indicating at least partial esterification. It has been noted [49, 50] that the introduction of amines promotes a shift of the equilibrium towards full esterification and the isolation of a product similar in composition to cellulose trinitrite.

III. Studies on the heterogeneous *O*-nitrosation of cellulose and its products

A comprehensive study of cellulose nitrite became possible after a way had been found of preparation it without impurities in a dry crystalline state. It has been suggested that mixtures of N_2O_4 with aprotic organic liquids, which do not dissolve cellulose nitrite, be used for the *O*-nitrosation of cellulose.[57, 64, 67–71] As in the preparation of solutions, the 'driving force' of the process is the increased affinity of the reaction medium for HNO_3. The use of DMF, DMSO, DMA, and ethyl acetate is possible only in the presence of an excess of N_2O_4 (> 30 vol.%), which rules out the dissolution of the reaction product. Absolute diethyl ether, which does not dissolve cellulose nitrite, proved to be the most suitable organic component. Diethyl ether has a fairly high affinity for HNO_3 [72, 73] (Table 1) and N_2O_4;[74, 75] it is suitable not only as a reaction medium but also as a medium for the subsequent removal of the sorbed nitrogen-containing substances from the final product. The high vapour pressure of diethyl ether ensures the ease and completeness of the drying of cellulose nitrite washed with this solvent.

In the study of the nitrosating activity of the N_2O_4 diethyl ether system it was established [68, 70] that, with increase in the concentration of N_2O_4 in the mixture to ~ 23 vol.%, the increase in the rate of reaction is small. This is followed by acceleration, which becomes very rapid starting from N_2O_4 concentration of ~ 37 vol. % (Fig 4). These N_2O_4 concentrations actually correspond to the stoichiometric molar compositions (1 : 2 and 1 : 1) of its complexes with diethyl ether.[75] As a consequence of the decomposition of the complexes, the system contains a certain amount of free N_2O_4, which permeates into the bulk of the fibre much more readily than the complexes. The 1 : 1 complex is less stable [75] and more dissociated. With increase in the N_2O_4 concentration above the stoichiometric value, the nitrosation process accelerates sharply. An increase in temperature tends to decrease the stability of the complexes with 'liberation' of N_2O_4 and its dissociation.[75] The reaction rate increases more than might have

Table 1. The donor numbers (DN) of the organic solvents employed and the enthalpies of their interaction with HNO_3 ($-\Delta H$).

Solvent	DN	$-\Delta H$ / kJ mol^{-1}
Pyridine	33.1	99.2
DMSO	29.8	52.5
DMF	26.6	60.2
Diethyl ether	19.2	29.8
Ethyl acetate	17.1	19.7

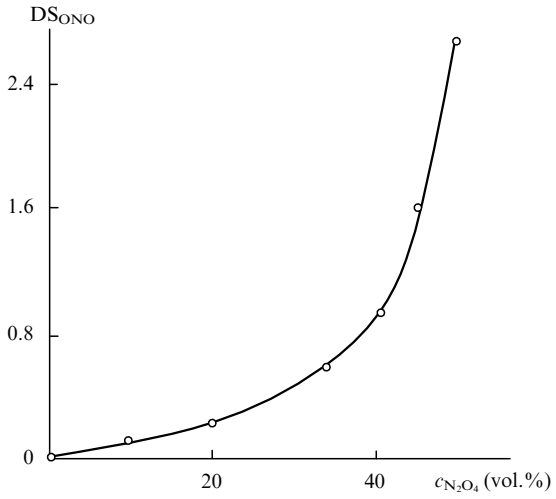


Figure 4. Dependence of the degree of nitrosation of cellulose on the N_2O_4 concentration in diethyl ether (reaction time 18 min, liquid modulus 50 ml g^{-1}, 0 °C).

been expected solely on the basis of the temperature coefficient of diffusion.[68, 70] Taking into account the high volatility of the components of the nitrosating mixture, it was recommended [67, 68, 70] that cellulose trinitrite be obtained in the presence of a higher N_2O_4 content (~ 50 vol. %) in diethyl ether but at reduced temperatures (~ 0 °C). The final product should be washed free of the sorbed components of the reaction medium with cooled absolute diethyl ether, the completion of the washing process being checked by means of the starch-iodine indicator. It is desirable that the preparation be dried by evacuation in the cold.

The nitrosation of cellulose takes place also in the absence of an electron-donating organic component.[68, 69] The excess N_2O_4 is capable of binding and removing from the reaction zone the HNO_3 produced, since it dissolves it with formation of fairly stable compounds.[76] The rapid intracrystallite permeation of the free N_2O_4 into the cellulose phase gives rise to a very high rate of reaction.[69] However, serious methodological, complications, associated with the occurrence of competing processes, arise in this case.[69]

The combination of diethyl ether with NOCl does not allow the preparation of a highly substituted cellulose nitrite.[57, 68] The electron-donating ability of diethyl ether is insufficient to bind the hydrogen chloride formed as a side product, which is a stronger acid than HNO_3. A mixture of chloroform with pyridine is suitable in this instance as the reaction medium. In contrast to diethyl ether, chloroform can dissolve and remove from the reaction zone the second reaction product, pyridine hydrochloride.

The sorbed components of the reaction medium can be removed from the reacted material also with water at 0–5 °C in the presence of bases such as, for example, pyridine or $NaHCO_3$ (pH ~ 8.5).[57, 69] A moist fibrous cellulose nitrite, stable in the cold and similar to the preparations isolated from solutions, is obtained.[44, 59]

Analysis of the products of the heterogeneous reaction for the nitrite and nitrate forms of nitrogen by the familiar chemical methods and also those proposed by Torgashov and coworkers,[57, 59, 68] demonstrated a satisfactory agreement among the results, indicating the vast predominance of the nitrite ester groups and the possibility of the attainment of a high degree of substitution up to complete substitution. Using the gravimetric analysis of a dry preparation (DS = 2.97) obtained with the aid of diethyl ether from chromatographic paper (97% α-cellulose), Torgashov et al.[57] tested, apart from the conclusion about the purity of the product, the hypothesis [15, 36, 61] that molecular complexes between cellulose and HNO_2 or nitrogen oxides with different degrees of oxidation are formed in the given systems. After nitrosation, washing, drying and regeneration, the specimen retained the form of a sheet, which is most convenient for studies. The molecular mass (M) of the elementary unit of the nitrogen-containing compound obtained was found from the gravimetric results:

$$M = 162\,\frac{m_1}{m_2},$$

where m_1 and m_2 are the masses of the reaction product and of the cellulose regenerated from it with water. The value M = 249.48 found was compared with the molecular masses of the postulated compounds (Table 2). The latter were calculated from the degree of substitution in terms of HNO_2. The minimum discrepancy between the experimental and calculated values corresponds to cellulose nitrite (DS = 2.97). For the remaining variants, the discrepancy greatly exceeds the possible errors of the gravimetric method. The formation of cellulose nitrite in the given systems and not of its isomeric *C*-nitroso-compound is demonstrated by the decomposition of the preparations obtained by $LiAlH_4$ or CaH_2 in anhydrous diethyl ether into ammonia and chemically unchanged cellulose.[57] *C*-Nitroso-compounds are known to be readily reduced to amino-derivatives.

The visible and UV spectra of the preparations obtained are identical with the spectra of the cellulose nitrite isolated from

Table 2. The calculated molecular masses of postulated compounds of different composition.

Compound	M	Absolute deviation	Relative deviation (%)
$C_6H_7O_2(OH)_{0.03}(ONO)_{2.97}$	248.13	+1.35	0.5
$C_6H_7O_2(OH)_3 \cdot 2.97HNO_2$	301.59	−52.11	20.9
$C_6H_7O_2(OH)_3 \cdot 2.97N_2O_4$	435.24	−185.76	74.5
$C_6H_7O_2(OH)_3 \cdot 2.97[N_2O_4 \cdot (C_2H_5)_2O]$	655.02	−405.54	162.5
$C_6H_7O_2(OH)_3 \cdot 1.485N_2O_3$	274.86	−25.38	10.2

Note. The absolute and relative deviations are quoted relative to the experimental molecular mass M of 249.48.

solution [59] and with the spectra of other organic nitrites (Fig. 5). The *4–5* band absorption in the range 330–380 nm characteristic of these compounds [66] vanishes when the preparation is treated with water or alcohol. A similar correspondence has been observed between the IR spectra of the heterogeneous interaction products and the highly substituted cellulose nitrite precipitated from solution.[15, 59] The spectrum of a solution of cellulose in DMSO presented in Fig. 2 corresponds to the preparation obtained with the aid of diethyl ether.

In a study of the crystal structure of cellulose trinitrite,[68–70, 77–80] special procedures,[68, 69, 79] ensuring the protection of the specimen against decomposition throughout the X-ray diffraction measurement,were used. Oriented preparations (DS = 2.93–2.97) were obtained from purified and bleached flax fibres (97% α-cellulose), which had been used successfully in previous [81, 82] X-ray diffraction analyses of cellulose nitrates.

The texture X-ray diffraction pattern of cellulose trinitrite (Fig. 6), (Table 3) contains 19 independent reflections, which have been satisfactorily indexed in terms of a monoclinic unit cell with the parameters a = 25.3 Å, b = 18.9 Å, c = 25.5Å (fibre axis), and γ = 95.8 °.[70, 79] Eight chain molecules pass through the unit cell. The theoretical density of the crystallites, calculated from these unit cell parameters, is 1.36 g cm^{-3}. The experimental density (1.39 g cm^{-3}), determined pyknometrically using absolute diethyl ether, agrees satisfactorily with the calculated value. In the determination of the density, the operations involving the nitrosation of cellulose with a N_2O_4–diethyl ether mixture and

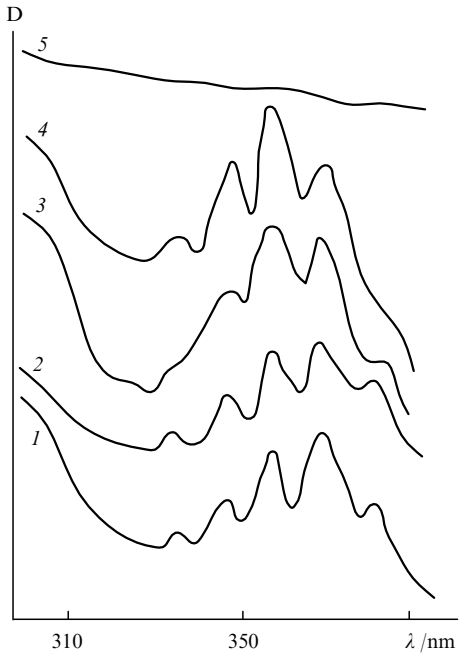


Figure 5. UV and visible spectra of *tert*-butyl nitrite (*1*), glycerol trinitrite (*2*), poly(vinyl alcohol) nitrite (*3*), cellulose nitrite (DS = 2.85) (*4*), and cellulose nitrite (DS = 2.85) after its interaction with alcohol (*5*).

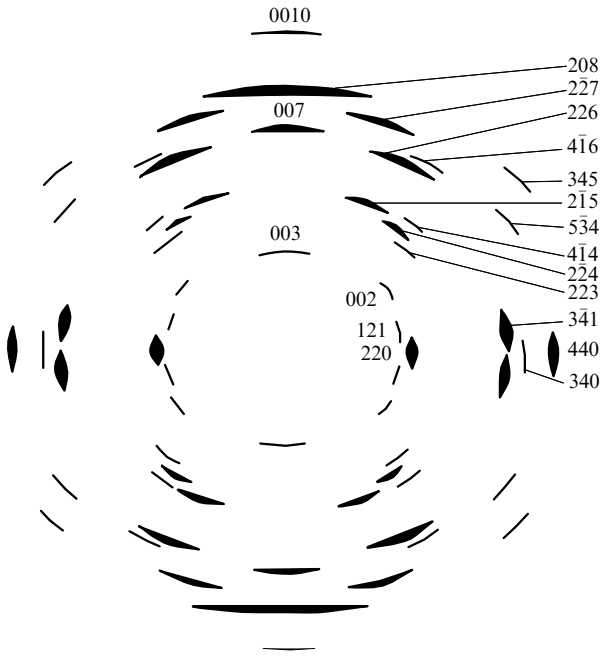


Figure 6. The indexing of the reflections on the texture X-ray diffraction pattern for cellulose trinitrite (DS = 2.97).

the washing of the final product with diethyl ether were performed directly in the pyknometer.[70, 79]

There is an evident analogy between the structures of the cellulose trinitrite crystallites and those of the 'related' cellulose trinitrate.[81–83] Both compounds are outstanding among the crystallographically investigated cellulose derivatives having a helical chain conformation with a five-unit pitch and hence with an 'anomalous' identity period of ~ 25.5 Å. In the crystallites of other cellulose triesters as well as cellulose itself, this parameter is

Table 3. The observed reflections and interplanar spacings (d) of cellulose trinitrite crystallites (Cu $K\alpha$ radiation, Ni filter).

hkl	d/Å		I[a]
	experiment	calculation	
220	7.10	7.19	v.s.
340	3.90	3.93	v.w.
440	3.55	3.59	s.
121	8.03	8.07	w.
3$\bar{4}$1	4.28	4.23	v.s.
022	7.55	7.57	v.w.
003	8.51	8.48	w.
223	5.40	5.49	w.
2$\bar{2}$4	4.93	4.97	m.
4$\bar{1}$4	4.43	4.43	w.
5$\bar{3}$4	3.49	3.47	v.w.
2$\bar{1}$5	4.66	4.63	m.
345	3.13	3.11	v.w.
2$\bar{2}$6	3.74	3.75	s.
4$\bar{1}$6	3.50	3.50	w.
007	3.65	3.60	m.
2$\bar{2}$7	3.31	3.33	m.
208	3.09	3.09	m.
010	2.55	2.55	v.w.

[a] The following designations for the intensities of the reflections have been adopted: v.s. — very strong; s. — strong; m. — medium; w. — weak; v.w. — very weak.

determined by the length of the cellulose fragment (~ 10.3 Å) regardless of the polymorphic modification.

Distinctive features have also been noted in the formation of the crystalline phases of the incompletely substituted nitrated and nitrosated cellulose.[69] The different contents of nitrogen in specimens of highly substituted cellulose nitrate causes certain differences in the unit cell parameters.[4, 82] Accordingly, the angular distribution of the reflections on the X-ray diffraction patterns of preparations with high but somewhat different degrees of substitution may not agree. In the case of cellulose nitrite, the dependence of the diffraction angles on the degree of substitution, the nature of the nitrosating agent (N_2O_4 or NOCl), and other factors is almost imperceptible.[69] On the diffractograms of preparations differing, apart from the degree of substitution (2.52–2.85), in the form of the initial native cellulose, the nitrosation conditions, and the conditions in the isolation of the product from the reaction mixture, the angular positions of the reflections are identical and the same as for cellulose trinitrite (Fig. 7). The above factors influence mainly the intensity and sharpness of the reflections.

For the same degree of substitution and preparation conditions, the nitrite of wood cellulose is consistently less crystalline than the nitrite of cotton or flax cellulose, since the crystal structure of its cellulose precursor is less ideal. The crystallinity of the cellulose nitrite obtained in diethyl ether, which is inert to it, is always higher than that of the preparation obtained in DMF or ethyl acetate, which do not dissolve this product solely by virtue of the excess of N_2O_4 in the system. The crystallinity of equally substituted cellulose nitrosation products increases in aliphatic carboxylic acids with increase in the length of the hydrocarbon group of the acid. The isolation of cellulose nitrite from the reaction medium with the aid of anhydrous CCl_4 or CH_2C1_2, which are indifferent to N_2O_4 and HNO_3, is accompanied by a decrease in the degree of substitution and crystallinity. In contrast to diethyl ether, these liquids do not have a stabilising effect and serve merely as a 'transporting agent' in the removal of excess reactants from the polymer phase. The quite distinct individuality of the diffractogram of cellulose nitrite makes it possible to employ the X-ray diffraction method for the detection of the

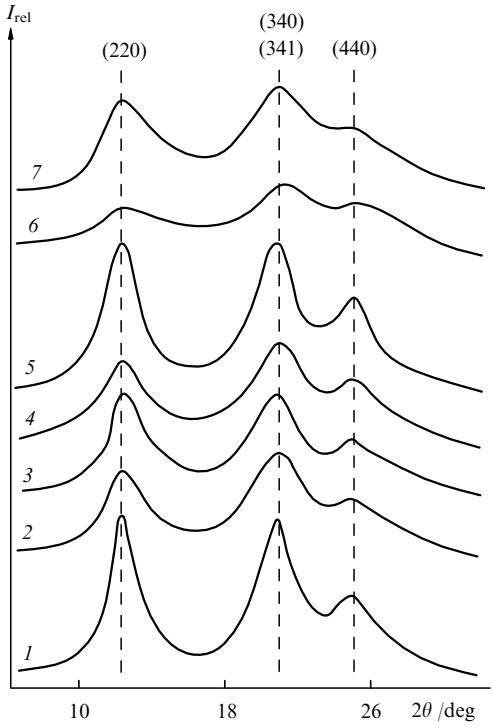


Figure 7. Diffractograms for isotropic cellulose nitrite specimens. Specimen: (*1*) DS = 2.85, obtained from cotton cellulose in N_2O_4–diethyl ether, isolated with diethyl ether, and dried *in vacuo*; (*2*) DS = 2.78, obtained from wood cellulose in N_2O_4–ethyl acetate, isolated with diethyl ether, and not dried; (*3*) DS = 2.81 obtained from cotton cellulose in N_2O_4–DMF, isolated with a water–pyridine mixture, and not dried; (*4*) as (*3*), but isolated with $NaHCO_3$ solution; (*5*) DS = 2.80, obtained from flax cellulose in N_2O_4–caprylic acid, and not dried; (*6*) DS = 2.52, obtained from cotton cellulose in N_2O_4–DMF, isolated with CCl_4 and CH_2Cl_2 in succession, and dried *in vacuo*; (*7*) DS = 2.75, obtained from cotton cellulose in $NOCl$–$CHCl_3$–pyridine, isolated with a solution of pyridine in $CHCl_3$, and not dried.

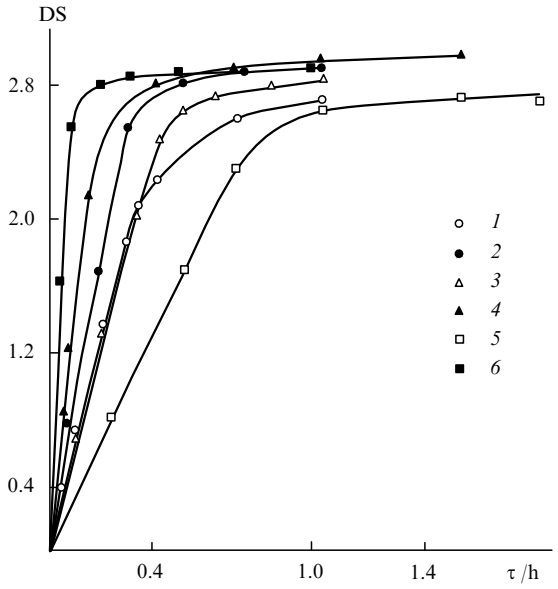


Figure 8. Kinetics of the heterophase nitrosation of cellulose under various conditions.
(*1*) N_2O_4–oenanthic acid (20 : 80), 26.5 °C; (*2*) N_2O_4–acetic acid (20 : 80), 26.5 °C; (*3*) N_2O_4–DMF (50 : 50), 0 °C; (*4*) N_2O_4–diethyl ether (50 : 50), 0 °C; (*5*) and (*6*) amorphised cellulose, N_2O_4–diethyl ether (10 : 90), 0 and 26.5 °C respectively.

crystalline phase of this compound in a complex reaction mixture, where other methods are inapplicable.[77,78]

The kinetics of the heterophase *O*-nitrosation of cellulose in organic media have been investigated taking into account the influence on the process exerted by the factors specific to the given systems.[68,70,84,85] Together with highly crystalline cellulose, a specimen with a more accessible structure, prepared by the decrystallisation of cellulose, was employed. It was obtained by heterogeneous regeneration from cellulose nitrite under anhydrous conditions.[84] The reaction in DMF, ethyl acetate, diethyl ether, and acetic and oenanthic acids (AA and OA respectively) was investigated. The kinetic curves (Fig. 8) were obtained for the minimal value of the liquid modulus established (50 ml g^{-1}), an increase in which hardly affects the degree of esterification.

The long linear section of the curves, reflecting the constancy of the rate at which an appreciable mass of cellulose (from 40% to 90%) is converted into the nitrite, is described by the zero-order equation

$$\alpha = k_0 t\,,$$

where α is the degree of conversion at time t and k_0 is the rate constant.

In heterogeneous reactions, this type of relation is attributed to the constancy of the reaction surface in the conversion of a large proportion of the initial substance.[86] Bearing in mind that the capillary mechanism of the transport of the reactant predominates in cellulose fibres over the diffusional mechanism,[87] the constancy of the cross-section of the reactant flux may be represented as the migration of the reaction zone at a constant rate via a network of capillaries. In this case, one has to assume that the reaction proceeds layer-by-layer with conversion of the main bulk of cellulose on the outer surface. The decrease in the area of the latter is responsible for the bending of the kinetic curve on passing to inner regions, accessible with difficulty, where truly diffusional transport plays the main role.

Taking into account the methodology of the familiar studies[88,89] on the topochemical reactions of cellulose, the experimental data (Table 4) were expressed quantitatively with the aid of the Erofeev–Kolmogorov equation

$$\alpha = 1 - \exp(-Kt^{\,n})\,,$$

where K and n are constants. The reaction orders n, determined from the slopes of the modified curves, indicate that the order is in all cases limited by chemical factors. The activation energies E are also too high for diffusional kinetics.[90] However, the inconstancy of the composition of the reaction mixture and of the state of the reacting surface, characteristic of the given systems, throw doubt on the conclusion concerning the rate-limiting stage reached from the analysis of topokinetic equations. The influence of the nature of the solvent and temperature on the rate of the complex formation reaction between the liquid components[74,75] was discussed above. The rate of the reaction depends on the nature of the organic medium even in mixtures rich in N_2O_4 (Table 4). The smallest change in the reaction surface as a result of swelling should occur during nitrosation in diethyl ether and acetic and oenanthic acids, which do not dissolve cellulose nitrite. The rate of reaction in diethyl ether, the basicity of which is higher than that of carboxylic acids, is higher than in acetic acid but lower than in oenanthic acid, although the basicities of both acids are virtually identical. This difference can be accounted for by taking into account the functional density of the medium (FDM), equal to the number of electron donors per unit volume.[84] The expression for this parameter includes the density (d, at 20 °C) and the molecular mass of the organic liquid:

$$\mathrm{FDM} = \frac{1000d}{M}\,.$$

Table 4. The conditions and kinetic parameters of the cellulose *O*-nitrosation reaction.

$c_{N_2O_4}$ (vol.%)	T/°C	A(%) [a]	k_0/h^{-1}	k/h^{-1} [b]	n	E /kJ mol^{-1} [c]
Organic medium — diethyl ether						
50	0	80	3.70	7.50	1.21	
40	0	75	1.07	2.26	1.36	
33	0	70	0.67	1.05	1.00	
20	0	70	0.26	0.41	1.25	
20	11.5	76	0.71	1.34	1.17	64; 69
20	15.0	75	1.10	2.21	1.30	
20	25.5	77	3.00	5.54	1.21	
10	0	40	0.05	0.07	1.02	
10	11.0	59	0.20	0.26	1.03	79; 77
10	25.5	67	0.88	1.34	1.14	
10	0 [d]	82 [d]	1.15 [d]	2.17 [d]	1.25 [d]	54 [d]; 58 [d]
10	25 [d]	90 [d]	8.50 [d]	19.70 [d]	1.21 [d]	
Organic medium — ethyl acetate						
50	0	70	1.43	2.22	1.06	
Organic medium — acetic acid						
50	0	60	1.58	2.70	1.20	
68	0	73	7.73	11.83	1.27	
62	0	70	4.00	7.32	1.23	
20	0	67	0.13	0.19	1.10	80; 81
20	26.5	83	3.13	6.18	1.38	
Organic medium — oenanthic acid						
20	0	73	0.17	0.27	1.16	70; 68
20	26.5	70	2.33	3.30	1.08	
40	0	74	3.77	7.90	0.94	
30	0	67	1.83	4.52	1.53	
Organic medium — DMF						
20	0	—	~4	—		
20	0	—	~24	—		60
50	0	77	2.18	3.75	1.15	

[a] The fraction of cellulose reacting in accordance with the equation $\alpha = k_0 t$. [b] Determined from K/h^{-n} with the aid of the Sakovich equation: $k = nK^{1/n}$. [c] Calculation by the Arrhenius equation; the first value corresponds to the values of k_0. [d] Values for specimens of amorphised cellulose.

The smallest number of moles per unit volume is actually a characteristic of oenanthic acid (Table 5), so that a greater fraction of N_2O_4 remains unbound in the latter compared with other media. The activation energy is higher in mixtures of N_2O_4 with acetic acid than in its mixtures with oenanthic acid (Table 4), since the dissociation of the complex is an endothermic process [74] and the FDM is higher for acetic acid . Accordingly, with increase in temperature the reaction in acetic acid is accelerated to a greater extent than in oenanthic acid. The viscosity of the medium also plays an important role; the viscosity of oenanthic acid is highest (Table 5). In mixtures of diethyl ether, acetic acid and oenanthic acid with a reduced N_2O_4 content, where the influence of the FDM is abolished by the excess of the solvent, the importance of transport factors increases. In the least viscous, diethyl ether, the rate of reaction at a relatively low N_2O_4 concentration (20 vol. %) is higher than in oenanthic acid medium of similar composition.

Table 5. The functional denisities of the medium (FDM) and the viscosities of the organic media employed.

Solvent	FDM/ mol litre^{-1}	γ/ cP
Diethyl ether	9.70	0.23
Acetic acid	17.50	1.21
Oenanthic acid	7.07	4.34
DMF	13.00	1.10
Ethyl acetate	10.21	0.46

The influence of the structural characteristics of cellulose on the process kinetics is manifested clearly in experiments with a decrystallised specimen.[84] As a consequence of the facilitation of mass transport, there is a significant increase in the rate constant and in the fraction of cellulose reacting at a constant rate, as the activation energy diminishes (Table 4). In DMF and ethyl acetate, which dissolve cellulose nitrite, a heterogeneous course and completion of the reaction are possible only in the presence of an excess of N_2O_4 (40 vol.% – 50 vol.%). The decrease in its concentration as a result of its consumption on nitrosation alters the nature of the interface, since the polymer swells. The reason for the hindrance of mass transport may be the formation of a gel-like layer, the viscosity of which is highest when ethyl acetate is employed.[15] A distinctive feature of these systems is the acceleration of the reaction following a decrease in the N_2O_4 concentration to ~ 20 vol.% and its completion by the complete dissolution of the material. The bareing of the reaction surface as a result of the dissolution of the reacted layer facilitates mass transport and accelerates the reaction (k_0 was estimated approximately in this case from the time for the total dissolution of the specimen).

The sensitivity of the reaction to factors which determine the transport of the reactant, the change in the properties of the reaction surface, and also the appreciably lower rate of interaction with N_2O_4 than for low-molecular-mass analogues [91] conflict with the conclusion that chemical inhibition, which follows from the value $n \geqslant 1$, takes place. A precondition of an adequate description of the process is, in particular, that the composition and homogeneity of the polymer phase be determined at different stages of the reaction. Analysis of the corresponding diffractograms (Fig. 9) indicates convincingly the layer-by-layer course of the process, throughout which the material remains crystalline. The intensification of the reflections due to cellulose trinitrite with increase in the degree of substitution is accompanied by the

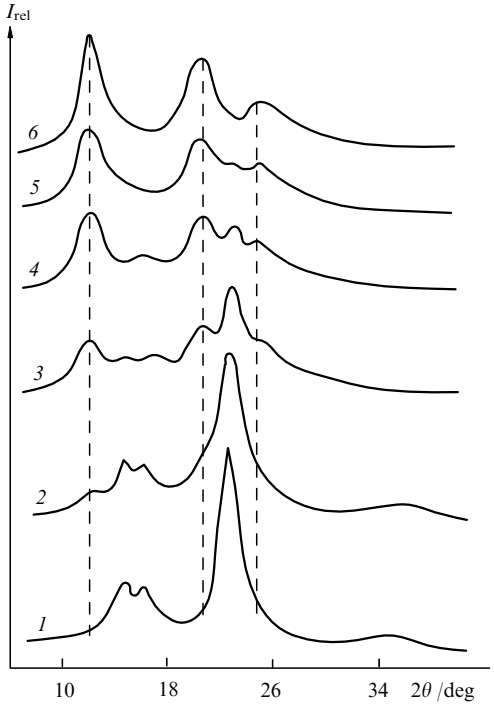


Figure 9. Dynamics of the structulral rearrangement at different stages of the nitrosation of cellulose with a N_2O_4 – diethyl ether (50 : 50) mixture at 0 °C.
DS: (*1*) 0.33; (*2*) 0.91; (*3*) 1.98; (*4*) 2.30; (*5*) 2.60; (*6*) 2.93.

synchronous weakening of the Cel-I reflections as far as their complete degeneration. The diffractograms of the products of the intermediate reaction stages resemble those of a mechanical mixture of the crystallites of Cel-I and its trinitrite. With the aid of ethyl acetate, which is indifferent to cellulose, it is possible to separate quantitatively a weakly substituted preparation (DS = 1.53) into a solution of highly substituted cellulose nitrite, and a virtually unaltered Cel-I.[84]

These data, together with those examined above (Fig. 7) clearly indicate the direct formation of the triester from cellulose, i.e. a high rate of the chemical reaction proper. In the kinetic reaction regime, a nearly statistical substitution of the OH groups, inducing the diffuseness of the X-ray diffraction patterns of the partly substituted preparations, would be most probable. By definition,[90] the set of the above features makes it possible to identify the *O*-nitrosation of cellulose in electron-donating organic media as a process occurring under the conditions of strong internal-diffusion inhibition in the 'external kinetic region'. The reaction is 'displaced' on to the outer surface and proceeds in a regime simulating the kinetic regime.

The highly substituted cellulose nitrite obtained as a result of heterogeneous processes with the aid of diethyl ether is a white substance with a yellowish tint. Its form corresponds to that of the initial cellulose (fibre, sheet, powder). In a moist atmosphere, it decomposes, readily with evolution of nitrogen oxides. Its resistance to the action of moisture increases appreciably in the pressed state.[68] The decomposition process is retarded in alkaline media.[70] On ignition, cellulose nitrite burns vigorously. The enthalpies of combustion and formation of cellulose nitrite, determined calorimetrically in the absence of contact with atmospheric moisture, are respectively -2970 ± 12.5 and -391 ± 12.5 kJ mol^{-1}.[92] The high heat of explosive decomposition (-3660 kJ kg^{-1}) and the large volume of the gases evolved on explosion (870 litre kg^{-1}) make it possible to classify cellulose nitrite as a fairly powerful explosive.

The N_2O_4- and HNO_3-free bright transparent solutions of cellulose nitrite in organic solvents are distinguished by a series of properties from the familiar solutions in nitrosating compositions.[93–96] Their lower viscosity makes it possible to attain a high polymer concentration (up to 15%). For example, the viscosity of a 6% solution of the nitrite of sulfate cellulose (DP = 1200) in ethyl acetate corresponds to the viscosity of a 2% solution in the N_2O_4–ethyl acetate mixture.[94] A similar rule is characteristic also of solutions of cellulose nitrate incorporated in graft copolymers of cellulose. The stability of joint solutions of cellulose nitrite and synthetic and artificial polymers is higher than that of analogous systems incorporating N_2O_4 and HNO_3. The absence of N_2O_4 and HNO_3 makes it possible to employ polymeric additives sensitive to them (polyamides and rubbers), expanding the possibilities for the moulding of the composite materials.[95]

Torgashov et al.[97] investigated the oxidation of cellulose nitrite (DS = 2.80) by N_2O_4 in carbon tetrachloride in order to test the hypothesis[2,28] that the nitrite ester participates as an intermediate in the reaction of preparation of monocarboxycellulose. The model cellulose nitrite was oxidised much more slowly than cellulose itself. The onset of the oxidation process was preceded by an induction period of ~ 6 h, during which neither denitrosation nor oxidation took place (Fig. 10). The reaction of cellulose under the same conditions began with the accumulation of nitrite ester groups in the first ~ 10 min, after which the oxidation process developed and the content of the nitrite groups diminished.

The behaviour of the model cellulose nitrite and the nitrite formed in the Cel–N_2O_4–CCl_4 system is not equivalent owing to the formation in the latter case of HNO_3, which, together with the destabilisation of the nitrite ester, increases the electrophilicity of N_2O_4[98] and hence its oxidising capacity. If 100% HNO_3 (3 moles per GPU) is added to the reaction mixture during the oxidation of cellulose nitrite, modelling the Cel–N_2O_4 system thereby, the rate of accumulation of carboxy-groups is found to be even higher

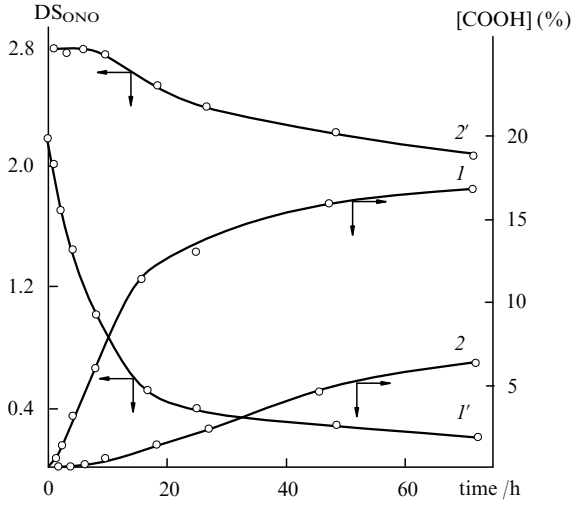


Figure 10. Variation of the contents of carboxy-groups (*1*, *2*) and nitrite ester groups (*1′*, *2′*) in the oxidation of cellulose (*1*, *1′*) and of its model nitrite ester (*2*, *2′*) with N_2O_4 in CCl_4.

than in the oxidation of cellulose. The formation of the labile cellulose nitrite at an intermediate stage of the oxidation process exerts a strong influence on the reaction, although, according to Sykes's data,[99] cellulose nitrite does not correspond to the intermediate in the cellulose oxidation reaction in terms of kinetic parameters.

IV. Heterophase structural transformations of cellulose with participation of labile nitrogen-containing derivatives

In the structural transformations taking place in the Cel–N_2O_4 system, the attention of investigators has been drawn to the effect of decrystallisation of native cellulose as a result of treatment with N_2O_4 and subsequent washing with water or an organic liquid.[100–106] The use of both liquid[101–105] and gaseous[100–106] N_2O_4 for this purpose has been discussed. The chemical composition of the decrystallised cellulose is unaltered, but the DP diminishes significantly (as far as ~ 300).[100,101,103]. The degree of decrystallisation and the accompanying degree of transformation of the native structural form into the Cel-II form were found to be extremely sensitive to the moisture content of the initial fibre and the conditions employed to perform the both stages of the process.[100,101,105,106] Such features of the process as the brief contact (~ 15 s) between cellulose and N_2O_4, which is sufficient for attainment of decrystallisation effect, or the suitability of water for washing of the treatment products, did not fit into the framework of the established ideas[107–109] about the mechanisms of the heterophase amorphisation of cellulose by reagents capable of inducing its intracrystallite swelling.

The interaction of cellulose with a N_2O_4 solution (18 vol. %–20 vol. %) in glacial acetic acid and subsequent washing of the fibre with the same acid ensure the formation of an amorphous structure with a capillary-porous system developed to the maximum extent and accompanied by a much smaller decrease in DP.[12,17,110,111] The cotton cellulose amorphised in this way is superior to the initial cellulose in terms of the water-retaining capacity (WRC) almost by a factor of 7 (250% against 37%).[12,111] Under identical conditions in hydrolysis in dilute HCl, the amorphised cellulose loses 84% of its mass, while the initial cellulose loses only 35%.[110,111] Complete acetylation of cotton cellulose after this treatment is 25 times faster than after standard activation with acetic acid alone.[112,113] For cellulose decrystallised directly by N_2O_4, the superiority of these and some other

parameters over the initial ones is manifested to a much smaller extent.[112, 114–117]

X-Ray-amorphous material with a high WRC (~ 250%) and a high hydrolysability has also been obtained by treating cellulose with more dilute (6 vol. % – 10 vol. %) N_2O_4 solutions in acetic anhydride or mixtures of the latter with acetic acid.[77, 118, 119] In contrast to the conditions indicated above, these reaction conditions induced the formation of a weakly substituted cellulose nitroacetate.

Kaputskii et al.[120] explained the amorphisation of cellulose by the irreversible destruction of the crystallites as a result of the intense swelling in the $N_2O_4 \rightleftarrows 2NO_2$ dynamic mixture. A decisive role was attributed to physical factors — sorption, condensation, dimerisation of NO_2 molecules, disjoining effect. However, it was found from the results of X-ray diffraction phase analysis that the competitive formation of two new crystalline phases takes place in the swelling stage.[121, 122] The X-ray diffraction expression for one of them corresponds to cellulose nitrite.[69] The second, more stable phase, is characterised by a diffraction pattern typical for Knecht's compound, the familiar adduct of cellulose with HNO_3.[30] The ratio of these phases in the swollen fibre depends on the moisture content in the initial cellulose, on the treatment conditions, and in particular on the access of atmospheric moisture to the reaction zone.[69, 121] The transformation of the structure of cellulose nitrite into that of KC under the influence of atmospheric moisture can be traced from the variation of the intensities of the corresponding reflections on the diffractograms of the fibre swollen in N_2O_4.[121–123]

The formation of cellulose nitrite in the reaction mixture was observed by X-ray diffraction [10, 121, 122, 124–126] before the X-ray pattern of individual cellulose nitrite became known.[78] The cellulose nitrite phase has been erroneously classified [10, 121, 122, 124–126] as a sorption compound on the basis of generally known principles [108, 127] of the structural reorganisation of cellulose under the action of other active nitrogen-containing reagents (ammonia, amines, HNO_3), which induce its intracrystallite swelling. These studies initiated a detailed investigation of the structural transformations possible in the given system.

Each of the above phases can be formed separately (cellulose nitrite or KC) by establishing an appropriate regime in the interaction of cellulose with liquid N_2O_4.[69, 128, 129] If the reaction conditions promote the removal from the fibre of HNO_3 formed and prevent the access of moisture from the surrounding medium to the reaction zone, cellulose nitrite is formed preferentially. A preparation having a typical cellulose nitrite diffractogram (Fig. 11) has been obtained by the successive treatment of air-dry cellulose (moisture content 5% – 7%) for ~ 2 min with three fresh portions of N_2O_4 whilst stirring and at a high value of the liquid modulus.[69, 129] The rapid protection of the preparation from atmospheric moisture immediately on completion of the treatment is obligatory, since otherwise the reflections of the second phase (KC) appear on the diffractogram. The crystallinity of the cellulose nitrite thus obtained is always significantly lower than that of the .substance obtained in the presence of an electron-donating liquid.

The combination of N_2O_4 with an electron-donating component (diethyl ether or acetic acid) pre-determines the nitrite pathway of the reaction and a higher stability of the cellulose nitrite swollen in the reaction medium.[69] On treatment with water, the crystalline phase of the nitrite of the native cellulose is readily reconverted into the crystalline Cel-I phase (Fig. 11).[68–70, 129] A direct relation has been traced between the degrees of crystallinity of the regenerated Cel-I and the precursor (the nitrite ester). The use of hot water or steam for the hydrolysis of cellulose nitrite tends to increase the crystallinity of the regenerated Cel-I.[68–70] The interconversion of the crystalline phases of Cel-I and its nitrite is characterised by more clear X-ray diffraction patterns than these obtained during the familiar heterogeneous cellulose esterification processes (acetylation, nitration) and in the hydrolysis of its triesters.[130] The conclusion [130] that the lattices of the initial

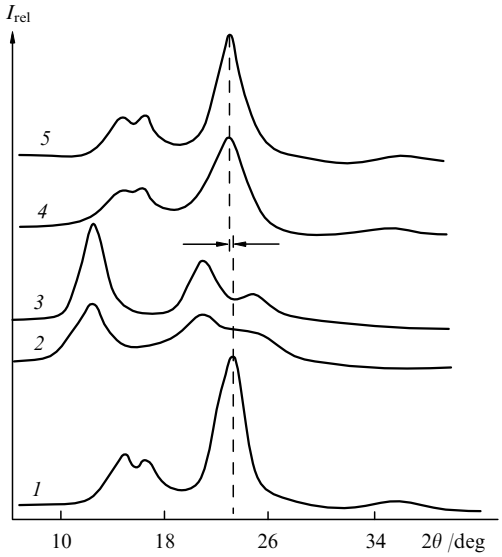


Figure 11. Equatorial diffractograms for the initial flax cellulose (*1*), highly substituted cellulose nitrite obtained with the aid of N_2O_4 alone (*2*) and a N_2O_4 – diethyl ether mixture (*3*), Cel-I regenerated with water from specimens *2* (*4*) and *3* (*5*).

native cellulose and that after a cycle of topochemical transformations are not quite equivalent has been confirmed. On the diffractogram of the latter, the (002) reflection is displaced by ~ 0.4 ° towards smaller diffraction angles (Fig. 11).[128–130]

The sorption-type KC is also a labile product of the interaction of cellulose with N_2O_4.[10, 69, 121, 123] The extremely scanty and contradictory information about its composition and structure is almost fully confined to the data in Refs 29 – 31, 131, and 132. This compound is formed in the reaction of cellulose with HNO_3 in the monohydrate form. As a rule, the acid concentration of 68 mass % – 69 mass % is employed. The azeotropic mixture corresponding to 68.4% HNO_3 is characterised by extremal physical properties [78] and a weak nitrating activity.[31, 131, 132] According to Gess,[131] KC is an oxonium compound, being a product of the addition of HNO_3 to the oxygen of the glucoside group of cellulose. The results of calorimetric measurements [133] have confirmed this view.

On the basis of the analysis of texture X-ray diffraction patterns and certain assumptions, Andress [30] proposed a monoclinic unit cell for KC with the following parameters: $a = 12.20$ Å, $b = 10.28$ Å (fibre axis), $c = 9.73$ Å, and $\beta = 53°$. Somewhat later Mark [132] assessed these data as reliable only with regard to the identity period. From the standpoint of the modern concept of the formation of cellulose adducts,[108, 127] the crystalline phase of KC should be regarded as a result of the insertion and stoichiometric 'fixation' of HNO_3 between the least interlinked (101) planes of the three-dimensional lattice of cellulose. The movement of these planes away from one another along the large *ac* diagonal (cell projection) is accompanied by a decrease in the angle β without affecting significantly the $(10\bar{1})$ and (002) planes (Fig. 12). The (101) reflection on the X-ray diffraction pattern of the new phase is displaced towards smaller diffraction angles. Andress identified this reflection as due to the (001) plane, emphasising at the same time the constancy of the $(10\bar{1})$ and (002) interplanar spacing in the transformation of the Cel-I lattice into the KC lattice.[30]

The KC lattice is formed in the interaction between cellulose and N_2O_4 under the conditions of the generation of HNO_3 from N_2O_4 directly in the swollen fibre.[10, 69, 121–123] The reactions of N_2O_4 with cellulose (nitrosation of cellulose) and also with the moisture in cellulose and in the surrounding medium (hydrolysis of N_2O_4) are the sources of the accumulation of HNO_3. For example, keeping of N_2O_4-impregnated air-dry cellulose in an atmosphere with a moderate relative humidity (50% – 60%) leads

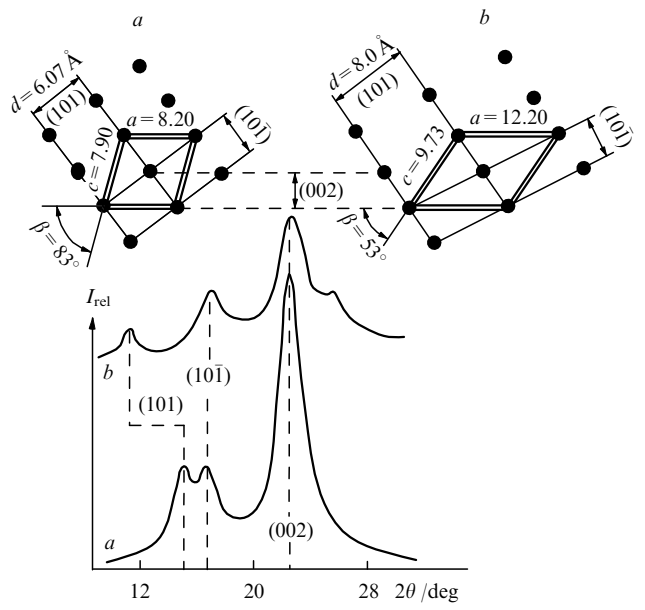


Figure 12. Schematic illustration of the transformation of the Cel-I unit cell (*a*) into the KC unit cell (*b*) and the corresponding changes in the diffractogram.

to the formation of KC. After only 15 min of the free evaporation of nitrogen oxides from the swollen fibre, the reflections due to cellulose nitrite vanish from its diffractogram [121] and the angular distribution in the reflections present [69, 121] corresponds exactly to that indicated by Andress [30] for the cellulose adduct with 68.6% HNO_3. The KC thus obtained is distinguished by an increased crystallinity and the corresponding well resolved X-ray diffraction pattern (Fig. 13). It is formed under the conditions of the decomposition of the cellulose nitrite formed initially, i.e. in a system with a weakened intermolecular interaction and an enhanced segmental mobility of the macromolecules. It is this peculiar 'chemical plasticisation' effect, that most probably creates favourable kinetic preconditions for the formation of the perfect KC crystal lattice.

It has been noted [128, 129] that the equatorial KC diffractogram changes somewhat with time (Fig. l3). After the specimen has been kept for 20 h under room conditions, the reflections at $2\theta = 11.2°$ and $22.8°$ are displaced to $2\theta = 12.0°$ and $24.0°$, indicating the densification of the crystallites. Judging from the meridional diffractograms,[128] the identity period remains unchanged (10.3 Å). Additional treatment with N_2O_4 of the specimen having the modified lattice under the previous conditions restores the initial diffractogram and improves somewhat the degree of its resolution. These observations suggest that KC is polymorphic, by analogy with alkaline cellulose.[127] The inconstancy of the KC crystal structure is apparently due to the change in its composition as a result of the evaporation of 'guest' molecules. According to Mark's data,[132] the adducts $C_2H_{10}O_5 \cdot HNO_3$ and $2C_6H_{10}O_5 \cdot HNO_3$ are characterised by indentical diffraction pattern. This is attributed to the presence in the former case of an excess of HNO_3, sorbed on the surfaces of the crystallites and not involved in the formation of the lattice. Postulating the involvement of partly oxidised cellulose macromolecules in the formation of KC, Urbanski and Zyszczyński [31] do not reflect the chemical changes in the formula quoted: $2C_6H_{10}O_5 \cdot HNO_3 \cdot H_2O$. Their conclusion that cellulose undergoes preliminary oxidation at the sixth carbon atom conflicts with many evident experimental results.[9] The specific feature of the structure of KC are still not understood. The possibility of increasing the amount of information derivable from the texture X-ray diffraction pattern of the KC obtained using N_2O_4 makes it possible to hope for a more rigorous quantitative description of the crystal structure of this compound.

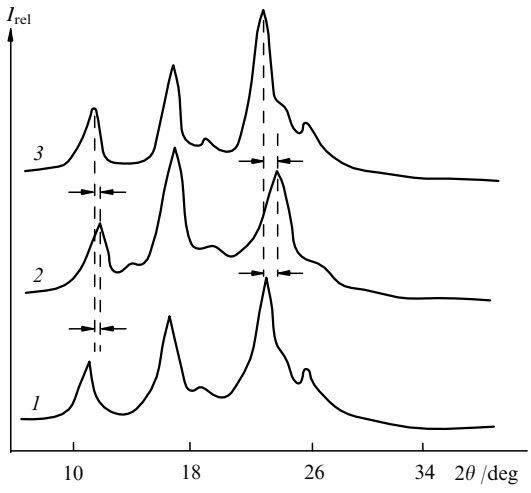


Figure 13. Equatorial diffractograms for KC obtained with the aid of N_2O_4 at a relative humidity of 53%.
(*1*) initial diffractogram; (*2*) after keeping specimen *1* under room conditions for 24 h; (*3*) after additional treatment of specimen *2* with N_2O_4 under previous conditions.

On treatment with water, the KC crystallites are always transformed into Cel-II crystallites.[9, 10, 131, 132] The mechanism and conditions of this transformation are on the whole similar to the usual mercerisation of cellulose.[77] The degree of the polymorphic transformation of Cel-I into Cel-II via KC reflects a measure of the involvement of the crystallites of the initial material in the adduct formation process.[9, 10] From the standpoint of permeating capacity, N_2O_4 has considerable advantages over 68% – 69% HNO_3.[10, 77]

The crystallinity of cellulose nitrite, and that of KC, can be logically regarded as naturally 'inherited' from the lattice of cellulose itself. In view of the lability of these derivatives, the application to them of the familiar artificial crystallisation procedures (for example, heat treatment) does not appear possible. Nevertheless, evidence for the spontaneous formation of the crystalline phases of both cellulose trinitrite [128, 129, 134] and KC [123, 134 – 138] has been obtained in experiments on cellulose known to be amorphous. The high extent of 'amorphness' of the initial model preparation, isolated from cellulose nitrite solution by special precipitation and regeneration methods,[139, 140] has been confirmed by the rapid and complete hydrolysability in dilute HCl. The cellulose trinitrite obtained from this preparation crystallised slowly on standing in the nitrosating medium (N_2O_4 – diethyl ether) even at 0 °C (Fig. 14). Two weak reflections (instead of one), distinguishing Cel-II trinitrite from Cel-I trinitrite, are gradually outlined on its diffractogram in the range $2\theta = 24 – 25°$.[128, 129] A similar difference between diffractograms is characteristic also of Cel-I and Cel-II trinitrates.[141] The decomposition of the specimens in cold water leads to Cel-II, while their decomposition by steam affords Cel-IV (Fig. 14). Instances of the formation of Cel-IV in the high-temperature saponification of stable Cel-II esters are known.[142] Thus amorphous cellulose can be converted into Cel-IV via its nitrite ester, an appreciable crystallisation effect being attained. Clearly, there can be no question of this type of ordering effect in chemically unaltered amorphous cellulose using treatment with hot steam for 1 min.

The crystallisation of amorphous cellulose as KG has been observed at room temperature on treatment with 68% HNO_3 and N_2O_4 under the conditions discussed.[123, 134 – 138] The use of N_2O_4 leads to an appreciably greater crystallisation effect, as in the experiments with the usual amorphous-crystalline cellulose.[121 128, 129] The process is extended in time, but has a distinct X-ray diffraction expression (Fig. 14). The kinetic causes of the

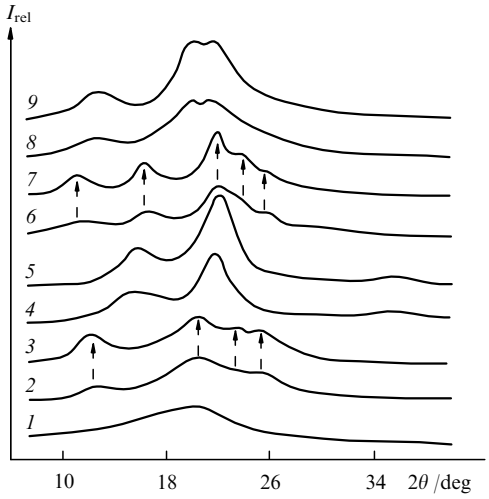


Figure 14. Diffractograms for isotropic specimens.
(*1*) initial amorphous cellulose; (*2*) and (*3*) trinitrite obtained from amorphous cellulose after being kept for 2 h (*2*) and 21 h (*3*) in a N_2O_4–diethyl ether mixture at 0 °C; (*4*) and (*5*) Cel-IV regenerated with steam from specimens *2* and *3* respectively; (*6*) KC obtained from amorphous cellulose (by treatment with 68% HNO_3 for 4 h); (*7*) KC obtained from amorphous cellulose (by treatment with N_2O_4 for 1 h, relative humidity 55%); (*8*) and (*9*) Cel-II regenerated with water from specimens *6* and *7*, respectively.

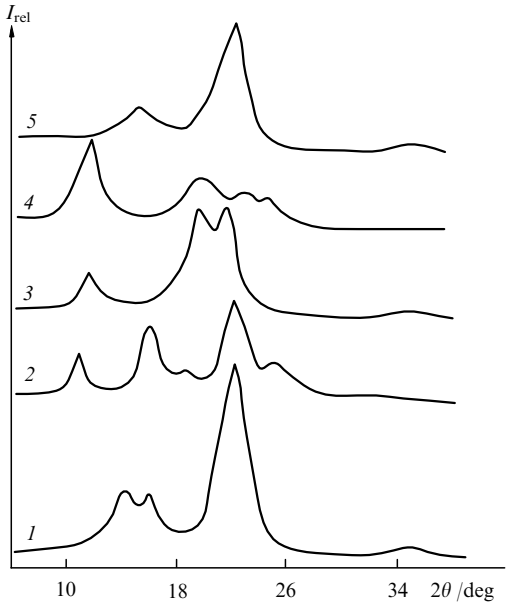


Figure 15. Equatiorial diffractograms obtained in succession for flax cellulose (*1*), Knecht's compound (*2*), Cel-II (*3*), Cel-II nitrite (*4*), and Cel-IV (*5*).
Conditions in the treatment of the specimen: (*1*) N_2O_4, relative humidity 53%; (*2*) H_2O, 20 °C; (*3*) N_2O_4–$(C_2H_5)_2O$; (*4*) H_2O, 100 °C.

phase transformation are evident, The weakening of the intermolecular interactions by the formation of an adduct and due to other factors [123, 136] stimulates crystallisation. Hitherto the formation of cellulose adducts (inclusion compounds) [108, 127] has been traditionally treated regardless of the amorphous regions of the fibre. In relation to KC, first data have been obtained [123, 134–138] concerning the possibility of the formation of crystallites of these compounds via a mechanism other than that [127] involving the insertion of 'guest' molecules in the finished lattice. Such a lattice is also produced as a result of the self-organisation of the unordered cellulose macromolecules bound to HNO_3. The crystallinity of KC attained during the self-organisation process is 'transmitted' to the Cel-II regenerated from this compound with water (Fig. 14). According to the results of a series of studies,[9, 123, 136, 138] the amorphous regions also perform a 'mediating' function, promoting the penetration of the reagent into the crystallites and the complete formation of a new crystalline phase. The participation of the amorphous regions in the formation of the crystalline phase of the cellulose adducts has been confirmed by the analogous experiments with alkaline cellulose.[136–138] However, the nonrigorous stoichiometry of the interaction in this system precludes a distinct X-ray diffraction expression of the crystallisation effect of the kind observed in the case of KC.

One of the characteristic features of the heterophase transformation of cellulose on treatment with N_2O_4 into a labile chemical or sorption derivative is the high crystallinity of the final reaction product. A high crystallinity is also characteristic of various polymorphic modifications of cellulose itself, regenerated with water from these labile compounds. The manifestation of this topochemical property has been illustrated [128, 129] by a series of diffractograms (Fig. 15), reflecting a series of consecutive transformations of cellulose on the same fibrous specimen If the initial Cel-I specimen is used and its treatment with N_2O_4 under appropriate conditions is alternated with treatment with water, then the following topochemical transformations can be observed on the basis of clear diffraction patterns:

Cel-I ⟶ KC ⟶ Cel-II ⟶ Cel-II trinitrite ⟶ Cel-IV.

Taking into account the above specific features of the formation of labile derivatives of cellulose and of its polymorphic transformations via these derivatives, one can account for the causes of the amorphisation of cellulose, which is possible under these conditions. The type of polymorphic modification of cellulose regenerated in water from the labile derivative depends on its nature. The formation of each labile compound separately in the interaction of cellulose with liquid N_2O_4 requires particular conditions for the accumulation and distribution of HNO_3 in the system.[129] The usual conditions in the preliminary treatment,[10, 101–105, 121] initiating both reaction paths at the intracrystallite level, lead to the regeneration of amorphous cellulose. Judging from the nature of the diffractogram (Fig. 16),[10 121 129] obtained in the stage involving the interaction of cellulose with N_2O_4, a product of the 'copolymer type' is formed in this case. The main bulk of the chain molecules are converted into a mixed

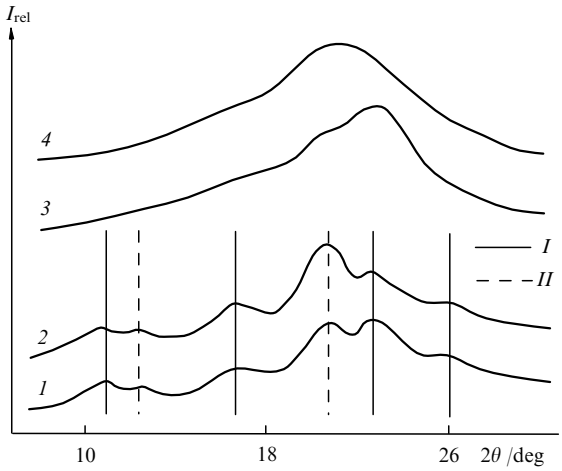


Figure 16. Diffractograms for isotopic flax cellulose specimens swollen in N_2O_4 (*1*), wood cellulose of the 'Raycord' brand (*2*), and the products of their interaction with water (*3*, *4*).
(*I*) KC; (*II*) cellulose nitrite.

derivative, losing their regular structure, which actually leads to a general disorganisation of the system (intense diffuse scattering on the diffractograms).

The uniform sequences of cellulose nitrite and KC units present in individual microvolumes form crystalline inclusions, the fraction of which is small (weak reflections against the background of diffuse scattering). The balance between cellulose nitrite and KC is unstable, the system tending to be wholly transformed into KC under the influence of small amounts of water, which actually occurs when it is absorbed from air with a humidity of 50% – 60%. Only the most unstable component (cellulose nitrite) decomposes under these conditions, stimulating the formation and crystallisation of KC. On rapid decomposition by an excess of water of both labile components simultaneously, the structural imperfection of the mixed cellulose derivative is 'transmitted' to the cellulose regenerated from it (Fig. 16). The elements of order in the cellulose decrystallised in this way are contributed by crystallite formations comprising cellulose nitrite and KC, which are transformed by the action of water into Cel-I and Cel-II respectively. Weak signs of crystallite scattering by these cellulose modifications are frequently manifested on the diffractograms of the amorphised specimens, which are on the whole diffuse.[101, 103, 114] A convincing demonstration of their presence in the amorphous 'matrix' follows from the diffractograms of the fraction of amorphised preparations which is difficult to hydrolyse.[105, 114] The degree of decrystallisation of cellulose increases appreciably when an undried organic solvent with a high affinity for nitrogen oxides and HNO_3, for example, diethyl ether or acetic acid, is used instead of water to wash the treated fibre.[10, 100, 101, 126] These regeneration conditions hinder the transformation of the crystalline cellulose nitrite and KC formations into the corresponding crystalline modifications of cellulose.

Brief contact (15 – 20 s) between air-dry cellulose and liquid N_2O_4 is favourable for amorphisation.[10] A short reaction time promotes the attainment of a disordered state of the system, limiting structure formation in the rapidly formed labile products. For example, the intracrystallite swelling of cellulose in 68% – 69% HNO_3 is known to be completed after $\sim$ 2 min,[9, 136] but an increase in the crystallinity of KC is observed over a period of many hours of contact between the fibre and the acid.[136]

The degree of amorphisation of cellulose depends on its moisture content and on the amount of moisture absorbed from the air by the fibre swollen in N_2O_4. It has been noted [105] that, in order to obtain X-ray-amorphous cellulose, the fibre interacting with N_2O_4 should contain at least 5% – 7% of water, i.e should be air-dry. The formation of KC participating in the amorphisation process is not alone in being coupled with the moisture content factor. For a high moisture content in cellulose or a high humidity of air, the process can also be influenced by the formation of N_2O_3 in accordance with the following equations:

$$N_2O_4 + H_2O \longrightarrow HNO_3 + HNO_2,$$

$$2HNO_2 \longrightarrow N_2O_3 + H_2O,$$

$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O,$$

$$2NO + N_2O_4 \longrightarrow 2N_2O_3.$$

A mixture of N_2O_4 and 3% – 10% of N_2O_3 is capable of effecting the transition of cellulose to the gel state or a solution.[13] The shrinkage and conversion into a gel-like formation of a bundle of cellulose fibres on wetting both with purified N_2O_4 under the conditions of a high relative humidity of air (92%) with and a mixture of the above nitrogen oxides (for a humidity of 53%), obtained by passing NO into cooled N_2O_4, has been noted.[129] According to an X-ray photodiffractogram, the chemically unaltered cellulose regenerated from the gel with water or alcohol is an isotropic amorphous material.[129] It is remarkable that such treatment of the fibre with N_2O_4 under the conditions of moderate humidity (50% – 60%) leads to the formation of the KC crystal lattice, from which textured Cel-II with a high degree of crystallinity can be readily regenerated with water.[10, 129] It is logical to assume the possibility of the local manifestation of the homogenisation effect for an increased moisture content in cellulose. Outwardly this may be undetectable owing to the presence of an excess of N_2O_4.

Cellulose dried beforehand is resistant to amorphisation by N_2O_4.[105, 126] After contact with N_2O_4 and washing with water, its structure corresponds to the Cel-I modification, as for the material generated with water from cellulose nitrite (Fig. 11). However, under conditions inducing the rapid nitrosation of air-dry cellulose [69, 129] the transformations of the 'dehydrated' cellulose on treatment with liquid N_2O_4 are extremely unusual. An idea about their dynamics is provided by the diffractograms presented in Fig. 17, which were obtained in the following readily reproducible experiment. A specimen comprising dried (105 °C, 2 h) flax cellulose fibres was treated with liquid N_2O_4 under conditions promoting esterification [69, 129] and was rapidly isolated from the external medium. This was followed by the repeated recording of X-ray diffractograms in the range of angles 8 – 25 °C at an equatorial scanning rate of 2 deg min^{-1}. Thus the recording of one diffractogram after another (Fig. 17) reflects the course of the structural changes in the fibre throughout approximately 1.2 h since the start of the recording. It follows from then that the rapid intracrystallite interaction of the 'dry' cellulose with N_2O_4 is characterised by a surprisingly high stoichiometry. The new unstable crystalline phase formed in the course of several minutes is distinguished by an individual angular distribution of the diffractogram reflections and by a higher degree of order than in cellulose itself, its trinitrite, or KC. According to the subsequent diffractograms, the crystal lattice of the initial phase approaches that characteristic of cellulose trinitrite as a result of continuous transformations. In the analogous experiments with an air-dry fibre, the diffractogram of cellulose trinitrite is obtained immediately (Fig. 11).[69, 129]

It may be postulated that a small amount of sorbed water stimulates the nitrosation of cellulose as a result of the ionisation of N_2O_4, whilst in the case of 'dehydrated' cellulose the process is extended over a period of time and it is possible to observe the diffractograms of the transition state adducts. At the same time the complex and varied nature of the interaction of cellulose with pure N_2O_4 does not rule out also other causes of the above transformations. The decisive influence of the moisture content factor on the transformations in the given system is evident, but has not been established in all its manifestations. Without taking into account this influence, seemingly identical reaction conditions may lead to different results.[114, 138]

The effectiveness of combining N_2O_4 with glacial acetic acid in the preparation of amorphous cellulose has already been noted.[12, 77, 110, 111] In the presence of carboxylic acids, the nitrosation of cellulose is not complicated by side reactions. According to series of X-ray diffraction features, the swelling of cellulose nitrite in carboxylic acids, (ranging from acetic to valeric) is an intracrystallite process.[77, 80, 124] The diffractograms of the preparations swollen in the esterifying mixture show, together with the reflections due to cellulose nitrite, an average-angle reflection (2θ = 6 – 7 °), which reflects the appearance in the lattice of a fairly extended ($\sim$13 Å) periodicity (Fig. 18) As a result of the displacement of the carboxylic acid from the esterified preparations by absolute diethyl ether, the above periodicity is eliminated, the swelling of the fibre diminishes appreciably, and the reflections due to the crystalline phase of cellulose trinitrite intensify. Such periodicity is also manifested when dry cellulose nitrite, prepared with the aid of diethyl ether, is acted upon by a carboxylic acid. With increase in the length of the hydrocarbon component of the acid molecule, the new interference shifts into the region of smaller angles.[77, 88] With increase in the degree of swelling of the preparation, its intensity increases synchronously with the degeneration of the (220) and (440) reflections due to cellulose nitrite (2θ = 12.4 ° and 24.8 °) and then, as the preparation decomposes, it diminishes to zero. The variation of the intensity of the reflection

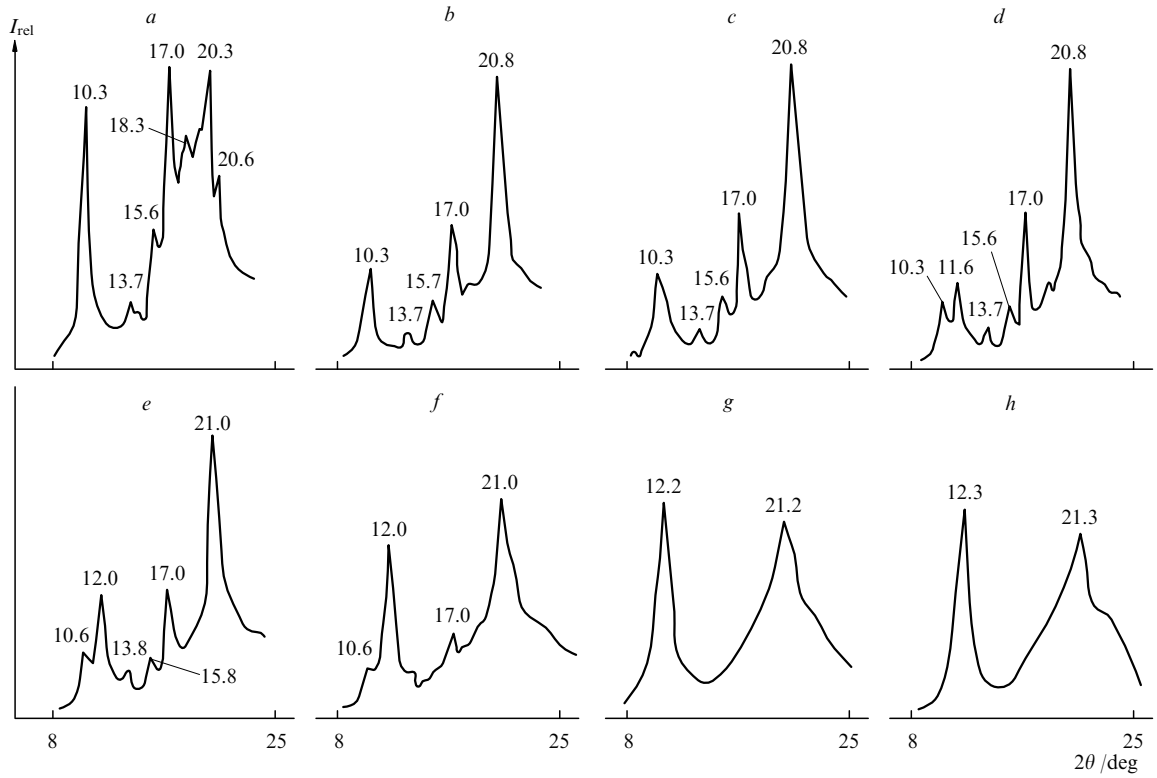


Figure 17. Dynamics of the structural rearrangement in the interaction of 'dry' cellulose with N_2O_4.
Time elapsed from the start of the experiment to the completion of the recording of the corresponding diffractogram (min): (*a*) 9; (*b*) 18; (*c*) 27; (*d*) 36; (*e*) 45; (*f*) 54; (*g*) 62; (*h*) 72.

due to cellulose nitrite also passes through an extremum at $2\theta = 20.8°$, the reflection shifting towards larger diffraction angles and becoming diffuse.[80] There is every reason to suppose that cellulose nitrite swells as a result of the insertion of the acid into the lattice between the (220) planes, the new periodicity appearing as a result of the planes 'moving apart'. Comparison of the increment in the (220) interplanar spacing with the sizes of the carboxylic acid molecules shows that this hypothesis is tenable.

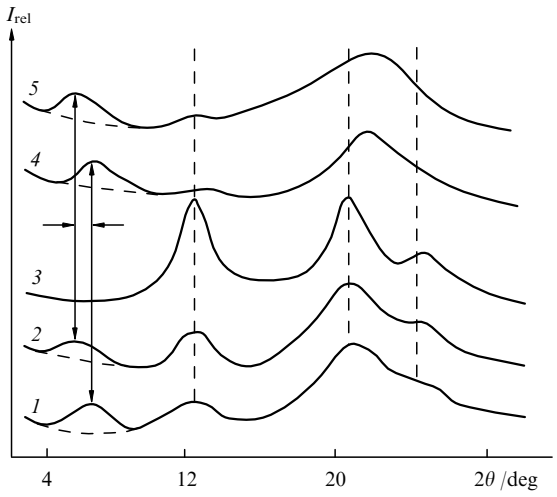


Figure 18. Diffractograms of the products of the interaction of cellulose nitrite with carboxylic acids.
Specimen: (*1*) specimen swollen in the N_2O_4–acetic acid esterifying mixture; (*2*) specimen swollen in the N_2O_4–butyric acid esterifying mixture; (*3*) specimen *1* after washing with absolute diethyl ether; (*4*) and (*5*) specimens swollen in acetic and butyric acids respectively.

The regeneration of cellulose during the washing of the esterified and swollen fibre with glacial acetic acid is actually its regeneration from the additive compound of cellulose nitrite with the acid under the influence of the moisture absorbed from air.[80] As a hygroscopic substance, glacial acetic acid functions as a moisture conductor, ensuring its equal access to the amorphous and crystalline regions of the swollen fibre. Denitrosation proceeds slowly, in accordancc with the statistical principle, introducing a structural disorganisation into the system. An appreciable decrystallisation effect can be attained by not allowing the decomposition of cellulose nitrite in acetic acid to go to completion, the process being stopped by washing with water, as a result of which structurally nonordered cellu1ose is rapidly and fully recovered from its partly substituted labile ester with an irregular structure. The direct action of water on the esterified preparation rules out the isolation of X-ray-amorphous cellulose.[77] Complete denitrosation in acetic acid gives rise to the greatest decrystallisation effect. This process, limited by the amount of sorbed moisture, can be greatly extended in time. Gert et al.[111] determined the degree of swelling of the fibre in acetic acid after the displacement of the latter with N_2O_4 from the product of the treatment of cellulose with a mixture of the above reagents, assuming that the swollen material comprises chemically unaltered amorphous cellulose. Tne value obtained (300%) exceeds the value of WRC (250%) established by the same gravimetric method after the displacement of acetic acid with water. The swelling of chemically unaltered cellulose in acetic acid cannot exceed its swelling in water. For the initial cellulose, the degrees of swelling are respectively 11% and 37%.[12,111] Evidently the swollen specimen employed for the analysis consisted of partly substituted cellulose nitrite, the decomposition of which was completed in the course of the drying of the sample.

The degree of decrystallisation of cellulose is very sensitive to the degree of swelling in the nitrosating mixture, i.e. to the mixture composition, temperature, and the reaction time.[12,77] Fig. 9 illustrates the effectiveness of the employment of different com-

positions of the acetic acid – N_2O_4 mixture for the decrystallisation of cellulose during 20 min interaction at the liquid modulus value of 20 ml g^{-1}. In all cases, identical conditions were maintained in the denitrosation reaction, which was stopped by the action of water. As can be seen, the use of mixture of acetic acid with 18 vol. % – 20 vol. % of N_2O_7 (5 mol of acetic acid per mole N_2O_4) at 30 °C makes it possible to amorphise cellulose almost entirely. This composition actually induces the highest degree of swelling, of the cellulose nitrite formed, since it exhibits a fairly high nitrosating activity at 30 °C (Fig. 8) At the same time, the composition includes an appreciable amount of free acid (the molar ratio in the acetic acid – N_2O_4 complex is 2 : 1; melting point 2 °C).[74] It is not fortuitous that the combination of N_2O_4 with a cellulose nitrite solvent (methyl acetate) is used in such proportion to disolve cellulose.[1,27] The change in this composition in any direction decreases sharply the decrystallisation effect, giving rise to an extremum in the variation under discussion (Fig. 19). The same behaviour is manifested also as a lower temperature of the 20 min treatment of cellulose with acetic acid – N_2O_4 mixtures of different composition. The weakening of the nitrosating activity leads in this case to a smaller degree of decrystallisation of celulose.A fairly rigorous correlation between the crystallinity index and the WRC of the preparations indicates that the measurements made are correct.

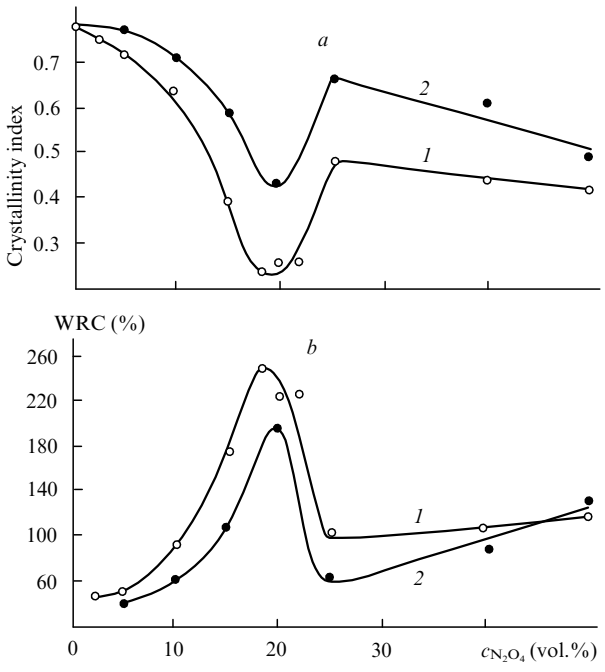


Figure 19. Variation of the crystallinity index (*a*) and the water retaining capacity (WRC) (*b*) of cotton cellulose as a result of treatment with N_2O_4 – acetic acid mixtures of different composition.
Treatment conditions: 20 min; liquid modulus 20 ml g^{-1}, temperature 30 °C (*1*) and 25 °C (*2*).

Thus the use of the acetic acid – N_2O_4 system for the preparation of amorphous cellulose is based on the specific features of the swelling and decomposition of cellulose nitrite in acetic acid.

V. Examples of the applied importance of labile nitrogen-containing polysaccharide derivatives

In this section, we shall confine ourselves to the discussion of certain rational approaches to the preparation of materials of practical importance, based on polysaccharides with participation of their labile derivatives. This methodology is based on the principle of the combined use of several functions of the reaction medium and of the unstable polymeric compound formed in it.

A good example is the homogeneous conversion of polysaccharides into sulfates in the DMF – N_2O_4 system by 'generated reactants' method.[143–146] The sulfates of accessible polysaccharides (cellulose, dextran, mannan, chitosan) possess a biological activity, like the expensive and difficult to isolate heparin, chondroitin sulfate, etc.[147] The most effective procedure for the uniform conversion of polysaccharides into sulfates is the homogeneous transesterification of the nitrites with the highly toxic and corrosive SO_3 in the DMF – N_2O_4 system.[16,17,50] It has been suggested[143–146] that the usual sodium and potassium salts of the acids $H_2S_nO_{2n+1}$ (n = 1, 2) or $H_2S_nO_{3n+1}$ (n = 1–3), which are themselves incapable of esterifying polyhydroxypolymers and function as 'stored' forms of SO_3, generating the latter on being acted upon by the reaction medium, be used for the formation of sulfates in the above system. Apart from homogenising the system as a result of the formation of the nitrite ester, the presence of N_2O_4 ensures the sulfating activity of the potential source of SO_3.

Reactants stimulating sulfate formation can act as oxidants, or can participate in exchange processes, or can combine the oxidising and exchange functions depending on the type of sulfur-containing compound employed. The first role is assumed when SO_2 is converted into the sulfating complex between SO_3 and the solvent.[148] The role of N_2O_4 is not restricted solely to the nitrosation of the polysaccharide and the generation of SO_3. The equilibrium degree of substitution as regards sulfo-groups depends on the ratio N_2O_4/SO_3, it diminishes with increase in the ratio.

Thus, apart from the known instability of sulfate esters in relation to acid media, account must be taken also of the desulfating activity of N_2O_4, i.e. the existence in the reaction systems of equilibrium between the sulfate and nitrite ester substitutents in the polysaccharide:

$$\mathrm{R-OH + N_2O_4 \rightleftharpoons R-ONO + HNO_3},$$
$$\mathrm{R-ONO + HNO_3 + SO_3 \longrightarrow R-OSO_3H + N_2O_4}. \qquad (6)$$

When salts of the acids $H_2S_nO_{3n+1}$ are used as the source of sulfur, the reactive sulfating agent is generated (*in situ*) as a result of the exchange activity of N_2O_4 and HNO_3

$$\mathrm{Na_2SO_4 + 2HNO_3 \rightleftharpoons H_2SO_4 + 2NaNO_3 \xrightarrow[-2NaNO_3]{N_2O_4}}$$
$$\mathrm{\longrightarrow SO_3 + HNO_2 + HNO_3\ (NOSO_3OH + HNO_3)},$$
$$\mathrm{2NOSO_3OH \xrightarrow{DMF} N_2O_3 + H_2S_2O_7 \cdot DMF},$$
$$\mathrm{H_2S_2O_7 \rightleftharpoons H_2SO_4 + SO_3}. \qquad (7)$$

The SO_3 evolved from the salts shifts equilibrium (6) towards the formation of the sulfate ester. By virtue of the homogeneity and reversibility of the process, the displacement of nitrite by sulfate ester groups takes place uniformly. The cellulose sulfates obtained dissolve fully in water even for DC = 0.2, which is not attained under any other known sulfate formation conditions.

A mixed type of the activating influence of N_2O_4 and HNO_3 is manifested in relation to salts of the acids $H_2S_nO_{2n+1}$:

$$\mathrm{Na_2SO_3 + 2HNO_3 \rightleftharpoons 2NaNO_3 + H_2SO_3 \xrightarrow{HNO_3\,(N_2O_4)}}$$
$$\mathrm{\longrightarrow H_2SO_4 + HNO_2\,(N_2O_3)}. \qquad (8)$$

It follows from Eqns (7) and (8) that, when salts with tetravalent sulfur are used, both exchange and oxidation reactions take place. The latter lead to heating of the system and the acceleration of the reaction. Salts with hexavalent sulfur are preferable because in this case the equilibrium is established slowly without heating, which creates 'mild' synthesis conditions and prevents degradative transformations of the macromolecules. The overall synthesis time is reduced as a result of the combination of the stages involving the dissolution of the starting material and its

conversion into a sulfate on simultaneous introduction of the polymer and the salt into the DMF – N_2O_4 mixture. The mannan and dextran sulfates synthesised in this way exhibit a distinct anticoagulant activity for the corresponding degrees of substitution but are not toxic even in large doses (2 – 5 g kg^{-1}).[149]

Partial nitrosation of cellulose in acetic acid may be of practical interest as an effective preactivation method in the preparation of cellulose acetates.[12, 113, 126, 150] The high reactivity of cellulose nitrite in the homogeneous transesterification reactions with acetylating agents is known.[8, 50] The proposed activation procedure reduces to brief treatment of cellulose with a solution of N_2O_4 in glacial acetic acid and subsequent displacement of the free nitrogen oxides from the fibre by the same acid.[112, 113, 126, 150] The traditional industrial schemes for the activation of cellulose are also based on the treatment of the fibre with acetic acid.[107, 151] The addition of small amounts of N_2O_4 (5 vol. %) does not induce excessive swelling of the fibre, so that the activation process is achieved simply and rapidly, achieving nevertheless an appreciable increase in reactivity (Table 6). After such activation, even mercerised cellulose, characterised by a low reactivity in acetylation, is acetylated almost wholly.[107] By carrying out the reaction up to the appearance of a 'clear field' in acetone, it is possible to obtain partially substituted cellulose acetates (DS = 2.12 – 2.26; DP = 420 – 590) soluble in acetone, dioxane, DMF, acetic acid, and other solvents.[126, 150] The properties of these products are similar to those of the secondary cellulose acetates obtained via a two-stage scheme: full acetylation of cellulose — partial homogeneous hydrolysis. The known methods for the direct synthesis of such materials[151, 152] are based on the acetylation of cellulose in the presence of large amounts of H_2SO_4 (15% – 25% of the mass of cellulose) and on the reaction being carried out in dioxane. The same 'chemical activation' principle (in the present instance, by conversion into a sulfate) is used. Such methods are more complex. The mixed esterification of cellulose leads to the homogenisation of the reaction mixture in early stages of the reaction and to uniformity of the substitution by acetyl groups, as a result of which the partly substituted cellulose acetate dissolves in organic solvents. In order to isolate cellulose acetate in a pure form and impart thermal stability to it,[153] a special operation involving the saponification of the sulfate ester groups is carried out. Analogous materials are prepared from partly nitrosated cellulose by means of an acetylating mixture having the usual composition and additional stabilisation procedures are not required.

In contrast to alkaline cellulose, Knecht's compound has not found a practical application. Nevertheless, when cellulose is processed in acid media, for example, for the preparation of its powdered forms, one can employ successfully the same properties of KC as those of alkaline cellulose. These are primarily the ability to induce the polymorphic transformation of cellulose and to serve as a reactive additive 'matrix' for chemical modification in accordance with a principle similar to that underlying the xanthogenation of alkaline cellulose.

It has been suggested[33, 154 – 157] that chemically unchanged microcrystalline Cel-II (MCCel-II) be obtained from native cellulose in accordance with a purely acid scheme, where HNO_3 performs the functions of both 'mercerising' and hydrolysing agents. After the interaction of cellulose with 68% – 69% HNO_3, the liquid is squeezed out of the swollen fibre and the strong acid remaining in it is diluted with water to a concentration of 5% – 15%, which ensures the selective hydrolytic cleavage of the fibrous system on subsequent heating. As a result of dilution, Cel-II is regenerated from KC and is then hydrolysed with the weak HNO_3 solution formed until the attainment of the 'limiting DP'. The simplicity and rationality of this scheme, eliminating the traditional mercerisation of cellulose with a solution of alkali, are evident. Furthermore, MCCel-II is obtained by the acid scheme with a lower crystallinity than the product formed by the alkaline-acid scheme.[156]

The reverse sequence of operations also leads to the 'mercerisation' effect, i.e. treatment of the MCCel-I obtained beforehand with 68% – 69% HNO_3 and then water. In this variant, there is the attractive possibility of attaining the virtually complete amorphisation of microcrystalline cellulose by increasing the duration of the reaction with 68% – 69% HNO_3 to 2 – 4 h.[32, 156, 158, 159] The main cause of decrystallisation is the uniform partial nitration of the microcrystalline cellulose. While possessing a low nitrating activity, 68% – 69% HNO_3 is nevertheless capable of esterifying cellulose to a slight extent (DC = 0.1 – 0.3) under the conditions of prolonged contact. The intracrystallite character of the swelling (the formation of KC) ensures the uniformity of the substitution by nitro-groups. The product isolated by treatment with water is weakly nitrated powdered decrystallised cellulose (PDC).

Powdered celluloses obtained by the above procedures are distinguished by high specific surfaces and sorption activities. (Table 7). In terms of the retention of water and the sorption of iodine and a dye, they are greatly superior to the microcrystalline cellulose prepared in the traditional way. It has been noted that HNO_3 in the form of the monohydrate, induces (like N_2O_4) the appearance of microcracks in the cellulose fibre. Their branched network has been observed on fibre cross-sections[77] and on the lateral surfaces of PDC particles[158] under a scanning electron microscope. The microcracks and the low crystallinity of the materials are responsible for the manifestation of strong sorption properties. The familiar bleaching activity of HNO_3 and nitrogen oxides[7, 8] is expressed by the high degree of whiteness of the powdered form of cellulose obtained with their aid.

The possibility of the effective employment of KC in the preparation of monocarboxycellulose, in particular its powdered forms, has been established.[34, 156, 160] The preactivation of native cellulose with 68% – 69% HNO_3 (the formation of KC) makes it possible to increase greatly the rate and uniformity of the subsequent oxidation in the same acid at a somewhat lower concentration (55% – 60%). The concentration of HNO_3 is reduced in the oxidation stage in order to weaken its nitrating activity. The oxidation reaction is initiated by the generation of nitrogen oxides from HNO_3. For this purpose, sodium nitrite is introduced into the system or the reaction temperature is increased. By virtue of preactivation, the fraction of the material oxidised at a high, virtually constant rate increases by a factor of 3 – 5,[160] which makes it possible to obtain rapidly uniformly oxidised cellulose, containing up to 17 mass % of carboxy-groups (the oxidation of the sixth carbon atom in all the GPU corresponds to 25.57 mass % of COOH groups). The bound nitrogen content in the specimens is 0.28 mass % – 0.46 mass %.[160]

At elevated temperatures, the cellulose oxidation and hydrolytic decomposition reactions coincide in time. Preactivation

Table 6. Results of acetylation by the methylene chloride method of cotton cellulose activated at 20 °C with acetic acid. or the N_2O_4 – acetic acid mixture followed by displacement with glacial acetic acid.

Acitvation conditions	Reaction time until attainment of clear field /min	DS of cellulose acetate	DP of cellulose acetate
Initial cellulose — native			
1 h, 80% AA	180	2.85	740
20 min, N_2O_4 – AA mixture (20 : 80)	7	2.86	400
5 min, N_2O_4 – AA mixture (5 : 95)	30	2.92	650
Initial cellulose — mercerised			
1 h, 80% AA	180 (no homogenisation)	1.62	
5 min, N_2O_4 – AA mixture (5 : 95)	50	2.90	

Note. Acetylating mixture: acetic anhydride – acetic acid – methylene chloride (30 : 10 : 60 vol.%), catalyst — perchloric acid (~1% of mass of cellulose), liquid modulus 10 ml g^{-1}, temperature 26 °C.

Table 7. Characteristics of powdered forms of cellulose.

Specimen	WRC [a]	Sorption/mg g^{-1}		DP	Degree of whiteness (%)
		I_2	Congo Red		
MCCel-I, FND brand (Filtrak Company)	43	19.0	288	180	95
MCCel-I, LT Brand (Lachema Company)	49	57.0	414	180	90
Sulfate MCCel-I (hydrolysis with 2.5 N HNO_3)	46 (48)	18.0	247	170	95
Sulfate MCCel-II, obtained by the alkaline-acid scheme	70 (117)	30.5		50	96
Sulfate MCCel-II, obtained by the acid scheme	81 (122)	151.0	550	50	98
PDC (2.2% N), obtained from sulfate MCCel-I	108 (182)	312.0		150	96
PDC (1.3% N), obtained from MCCel-I, LT brand (Lachema Company)	95 (156)	238.0	640	150	94

[a] The number in brackets characterises the water-washed final product before drying.

accelerates sharply both reactions. The hydrolysis of cellulose itself stimulates the oxidation reaction, because its products have a reductive function, promoting the formation of nitrogen oxides in the system. It is important to balance these reactions in such a way that the degree of hydrolysis does not affect negatively the yield of powdered oxidised cellulose.[160]

Oxidation of preliminarily dispersed cellulose, for example, microcrystalline cellulose, in accordance with this scheme, should be carried out at normal or reduced temperatures, initiating the reaction by adding N_2O_4 or sodium nitrite. There are virtually no mass losses in this case. By virtue of preactivation, the reaction from its very beginning, takes place also in the crystallites themselves and not only on their surfaces, so that the final products are characterised by a low degree of structural order even for a relatively low degree of oxidation.[160]

References

1. F N Kaputskii, Doctoral Thesis in Chemical Sciences, Institute of Chemistry of Wood, Riga, 1983
2. V A Koleno, Z Sh Sharshenalieva, E N Tarasova, A Moldoshev, N Ya Kuznetsova, V I Ivanov *Okislitel'nye Prevrashcheniya Tsellyulozy i ee Proizvodnykh* (Oxidative Transformations of Cellulose and Its Derivatives) (Frunze: Ilim, 1984)
3. A P Zakoshchikov *Nitrotsellyuloza* (Nitrocellulose) (Moscow: Gos. Izd. Oboron. Prom., 1950)
4. R I Sarybaeva, L S Shchelokhova *Khimiya Azotnokislykh Efirov Tsellyulozy* (The Chemistry of Nitric Acid Esters of Cellulose) (Frunze: Ilim, 1985)
5. I P An, M M Imanov *Khim. Drevesiny* (6) 47 (1985)
6. G M Korneva, A B Baskina *Initsiirovannaya Destruktsiya Tsellyulozy* (Initiated Destruction of Cellulose) (Frunze: Ilim, 1985)
7. O Kordsachia, D L Wang, R Patt *Papier* **39** 313 (1985)
8. J Rutkowski, K Perlinska-Sipa *Cellul. Chem. Technol.* **28** 35 (1994)
9. M V Shishonok, E V Gert, T I Filanchuk, F N Kaputskii *Zh. Prikl. Khim.* **60** 1153 (1987)[a]
10. E V Gert, A Sokarras Morales, M V Makarenko, F N Kaputskii *Khim. Drevesiny* (5) 56 (1983)
11. E V Gert, F N Kaputskii, D D Grinshpan, A P Bobrovskii *Zh. Prikl. Khim.* **49** 860 (1976)[a]
12. M V Shishonok, E V Gert, F N Kaputskii, Z V Stashenok *Khim. Drevesiny* (1) 38 (1982)
13. S M Hudson, J A Cuculo *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **C18** 1 (1980)
14. L K Golova, V G Kulichikhin, S P Papkov *Vysokomol. Soedin., Ser. A* **28** 1795 (1986)[b]
15. D D Grinshpan, *Nevodnye Rastvoriteli Tsellyulozy* (Nonaqueous Solvents for Cellulose) (Minsk: Izd. Universitetskoe, 1991) p. 223
16. R G Schweiger *TAPPI Notes* **57** 86 (1974)
17. B Philipp, W Wagenknecht *Cellul. Chem. Technol.* **17** 443 (1983)
18. P Manson, L Westfeld *Cellul. Chem. Technol.* **14** 13 (1980)
19. D D Grinshpan, F N Kaputskii, E V Gert, I N Ermolenko, M A Titov, I A Kovalev, I F Aleksandrovich *Dokl. Akad. Nauk. Belorus. SSR* **20** 531 (1976)
20. F N Kaputskii, D D Grinshpan, E V Gert, A P Bobrovskii, T A Savitskaya, N G Tsygankova *Vestn. Belorus. Univ., Ser. 2* (3) 14 (1976)
21. F N Kaputskii, D D Grinshpan, E V Gert, T A Savitskaya, A P Bobrovskii *Khim. Volokna* **2** 62 (1977)
22. A V Bil'dyukevich, E V Gert, V E Protsenko, F N Kaputskii *Khim.-Farm. Zh.* (6) 753 (1986)[c]
23. F N Kaputskii, A V Bil'dyukevich, V I Torgashov, E V Gert *Zh. Prikl. Khim.* **62** 131 (1989)[a]
24. A V Bil'dyukevich, V I Torgashov, E V Gert, F N Kaputskii *Vysokomol. Soedin., Ser. A* **31** 2580 (1989)[b]
25. F N Kaputskii, E V Gert, T A Savitskaya, D D Grinshpan *Vysokomol. Soedin., Ser. B* **21** 357 (1979)[b]
26. S N Ushakov *Efiry Tsellyulozy i Plasticheskie Massy na ikh Osnove* (Cellulose Esters and the Plastics Based upon Them) (Leningrad; Moscow: Goskhimizdat, 1941)
27. D D Grinshpan, Candidate Thesis in Chemical Sciences, Belorussian State University, Minsk, 1978
28. I N Ermolenko *Spektroskopiya v Khimii Okislennykh Tsellyuloz* (Spectroscopy in the Chemistry of Oxidised Celluloses) (Minsk: Izd. Akad. Nauk Belorus. SSR, 1959)
29. E Knecht *Berichte* **37** 549 (1904)
30. R K Andress *Z. Phys. Chem.* **136** 279 (1928)
31. T Urbanski, S Zyszczyński *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **13** 377 (1965)
32. USSR P. 1 432 062; *Byull. Izobret.* (38) 78 (1988)
33. USSR P. 1 481 234; *Byull. Izobret.* (19)102 (1989)
34. USSR P. 1 810 353; *Byull. Izobret.* (15) 52 (1993)
35. P Nicolardot, G Chertier *C. R. Acad. Sci.* **151** 719 (1910)
36. W F Fowler, C C Unrich, P A McFee, W O Kenyon *J. Am. Chem. Soc.* **69** 1636 (1947)
37. Fr. P. 1 469 890; *Chem. Abstr.* **68** 41 234b (1968)
38. Can. P. 979 577; *Chem. Abstr.* **84** 166 551 (1976)
39. BRD P. 2 530 451; *Chem. Abstr.* **84** 193 703y (1976)
40. H Ocakadsy *Fiber Sci. Ind. Jpn.* **4** 128 (1971)
41. L P Clermont *Can. Dep. Forest Bi-Mon. Res. Notes* **26** 58 (1970)
42. L P Clermont, F Bender *J. Polym. Sci., Polym. Chem. Ed.* **10** 1669 (1972)
43. A Vankateswaran, L P Clermont *J. Appl. Polym. Sci.* **18** 133 (1974)
44. R G Schweiger *J. Org. Chem.* **41** 90 (1976)
45. B Philipp, H Schleicher, W Wagenknecht *Cellul. Chem. Technol.* **9** 265 (1975)
46. W Wagenknecht, B Philipp, H Schleicher, I Beierlein *Faserforsch. Techtiltechn.* **28** 421 (1977)
47. W Wagenknecht, B Philipp *Faserforsch. Techtiltechn.* **29** 645 (1978)
48. B Philipp, H Schleicher, W Wagenknecht *Cellul. Chem. Technol.* **12** 529 (1978)
49. J Nehls, W Wagenknecht, B Philipp *Acta Polym.* **37** 610 (1986)
50. B Philipp, B Lukonoff, H Schleicher, W Wagenknecht *Z. Chem.* **26Jg** 50 (1986)
51. J Akira, J Atsushi, N Junso *J. Soc. Fiber Sci. Technol.* **42** T654 (1986)
52. M Pasteka, D Mislovikova *Cellul. Chem. Technol.* **9** 325 (1975)
53. D Mislovikova, M Pasteka *Cellul. Chem. Technol.* **11** 115 (1977)
54. K Clusins, M Vecehi *Helv. Chem. Acta* **36** 930 (1953)
55. N S Bayliss, D W Watts *Aust. J. Chem.* **9** 319 (1956)
56. D J Millen, D Watson *J. Chem. Soc.* 1369 (1957)
57. V I Torgashov, E V Gert, A V Bil'dyukevich, F N Kaputskii *Khim. Drevesiny* (1) 14 (1988)

58. B N Kondrikov, in *Teoriya Vzryvchatykh Veshchestv* (Theory of Explosives) (Moscow: Gosnauchtekhizdat – Oborongiz, 1963) p. 296
59. V I Torgashov, A V Bil'dyukevich, E V Gert, F N Kaputskii *Vysokomol. Soedin., Ser. B* **26** 632 (1984)[b]
60. K Nakanishi *Infrared Absorption Spectroscopy* (Tokyo: Holden-Day, 1962)
61. G M Laisha, V I Sharkov *Vysokomol. Soedin., Ser. A* **17** 999 (1975)[b]
62. USSR P. 1 131 882; *Byull. Izobret.* (48) 88 (1984)
63. V G Tsvetkov, A V Ivanov, V V Sokolov, Yu A Aleksandrov *Zh. Prikl. Khim.* **56** 501 (1983)[a]
64. E V Gert, V I Torgashov, A V Bil'dyukevich, in *Vsesoyuz. Konf. "Khimiya, Tekhnologiya, Primenenie Tsellyulozy i ee Proizvodnykh", Cherkassy (Tez. Dokl.)* [All-Union Conference 'Chemistry, Technology, and Applications of Cellulose and Its Derivatives', Cherkassy (Abstracts of Reports)] (Vladimir: All-Union Synthetic Resins Research Institute , 1985) p. 138
65. F N Kaputskii, A V Bil'dyukevich, V I Torgashov, E V Gert, in *Tez. Dokl. IV Vsesoyuz. Konf. po Membrannym Metodam Razdeleniya Smesei* (Abstracts of Reports at the Fourth All-Union Conference on Membrane Methods for the Separation of Mixtures) (Moscow: Mendeleev Moscow Chemical Engineering Institute, 1987) Part 2, p. 53
66. R N Haszeldine, J Jander *J. Chem. Soc.* 691 (1954)
67. USSR P. 1 237 672; *Byull. Izobret.* (22) 118 (1986)
68. V I Torgashov, E V Gert, A V Bil'dyukevich, F N Kaputskii *Vysokomol. Soedin., Ser. B* **29** 699 (1987)[b]
69. E V Gert, V I Torgashov, A V Bil'dyukevich, M V Shishonok, F N Kaputskii *Khim. Drevesiny* (2) 26 (1988)
70. E V Gert, V I Torgashov, F N Kaputskii *J. Polym. Sci., Part C, Polym. Lett.* **27** 393 (1989)
71. E V Gert, V I Torgashov, M V Shishonok, F N Kaputskii, in *Tez. Dokl. IV Vsesoyuz. Konf. po Fizike i Khimii Tsellyulozy* (Abstracts of Reports at the Fourth All-Union Conference on the Physics and Chemistry of Cellulose) (Minsk: Institute of Physics, Academy of Sciences of the Beloruss. SSR, 1990) p. 211
72. A P Kreshkov *Analiticheskaya Khimiya Nevodnykh Rastvorov* (Analytical Chemistry of Nonaqueous Solutions) (Moscow: Khimiya, 1982)
73. V G Tsvetkov, G N Marchenko, V F Sopin, L Ya Tsvetkova *Zh. Obshch. Khim.* **55** 233 (1985)[d]
74. W L Jolly, in *Preparative Inorganic Reactions* Vol. 1 (New York: Interscience, 1964)
75. C C Addison, J C Sheldon, B S Smith *J. Chem. Soc.* 999 (1974)
76. V I Atroshchenko, S I Kargin *Tekhnologiya Azotnoi Kisloty* (Nitric Acid Technology) (Moscow: Khimiya, 1970)
77. M V Shishonok, Candidate Thesis in Chemical Sciences, Belorussian State University, Minsk, 1985
78. E V Gert, V I Torgashov, A V Bil'dyukevich, in *Vsesoyuz. Konf. "Khimiya, Tekhnologiya, Primenenie Tsellyulozy i ee Proizvodnykh", Cherkassy (Tez. Dokl.)* [All-Union Conference 'Chemistry, Technology, and Application of Cellulose and Its Derivatives', Cherkassy (Abstracts of Reports)] (Vladimir: All-Union Synthetic Resins Research Institute , 1985) p. 139
79. V I Torgashov, D Ya Tsvankin, E V Gert *Vestn. Belorus. Univ., Ser. 2* (1) 68 (1989)
80. E V Gert, V I Torgashov, M V Shishonok, F N Kaputskii *Khim. Drevesiny* (3) 31 (1988)
81. A F Sviridov, R M Myasnikova, E F Titova, D Ya Tsvankin, A I Pertsin *Kristallografiya* **29** 247 (1984)[e]
82. A F Sviridov, D Ya Tsvankin, A I Pertsin *Vysokomol. Soedin., Ser. A* **26** 1553 (1984)[b]
83. D Meader, E D T Atkins, F Happey *Polymer* **19** 1371 (1978)
84. V I Torgashov, E V Gert, A V Bil'dyukevich, F N Kaputskii *Vysokomol. Soedin., Ser. A* **32** 266 (1990)[b]
85. V I Torgashov, E V Gert, F N Kaputskii, in *Vsesoyuz. Konf. "Khimiya i Reaktsionnaya Sposobnost' Tsellyulozy i ee Proizvodnykh" (Tez. Dokl.)* [All-Union Conference 'Chemistry and Reactivity of Cellulose and Its Derivatives' (Abstracts of Reports)] (Frunze: Institute of Organic Chemistry, Academy of Sciences of the Kirg. SSR, 1991) p. 179
86. M E Brown, D Dollimore, A K Galwey *Reactions in the Solid State* (Amsterdam: Elsevier, 1980)
87. S P Papkov, in *Fizicheskie i Piziko-Khimicheskie Aspekty Aktivatsii Tsellyulozy (Tez. Dokl.)* [Physical and Physicochemical Aspects of the Activation of Cellulose (Abstracts of Reports)] (Riga: Zinatne, 1981) p. 5
88. R I Sarybaeva, G N Osmonkanova, L S Shchelokhova, in *Khimiya i Fiziko-Khimiya Tselyulozy* (The Chemistry and Physical Chemistry of Cellulose) (Ed. V A Afanas'ev) (Frunze: Ilim, 1984) p. 103
89. N I Klenkova, O S Bludova, N A Matveeva, L A Volkova *Cellul. Chem. Technol.* **16** 615 (1982)
90. G M Panchenko, V P Lebedev *Khimicheskaya Kinetika i Kataliz* (Chemical Kinetics and Catalysis) (Moscow: Khimiya, 1985)
91. W Langenbeck, M Richter *Chem. Ber.* **B89** 202 (1956)
92. V I Torgashov, E V Gert, V V Simirskii, in *VI Vsesoyuz. Konf. "Termodinamika Organicheskikh Soedinenii" (Tez. Dokl.)* [The Sixth All-Union Conference 'Thermodynamics of Organic Compounds' (Abstracts of Reports)] (Minsk: Belorussian State University, 1990) p. 78
93. USSR P. 1 110 830; *Byull Iizobret.* (32) 81 (1984)
94. USSR P. 1 171 460; *Byull Iizobret.* (29) 103 (1985)
95. USSR P. 1 206 281; *Byull Iizobret.* (3) 95 (1986)
96. E V Gert, V I Torgashov, M V Shishonok, F N Kaputskii, in *Tez. Dokl. Vsesoyuz. Nauchno-Tekhn. Konf. "Osnovnye Napravleniya i Koordinatsiya Rabot v Oblasti Khimii Drevesiny do 2000 Goda"* (Abstracts of Reports at the All-Union Scientific and Technical Conference 'Fundamental Trends and Coordination of Studies in the Chemistry of Wood up to 2000') (Leningrad: VNPO Bumprom, 1988) Part 1, p. 99
97. V I Torgashov, E V Gert, A V Bil'dyukevich, F N Kaputskii *Khim. Drevesiny* (4) 38 (1988)
98. S Lunn, D M Mason, W H Corcoran *J. Phys. Chem.* **59** 238 (1955)
99. P Sykes *A Guidebook to Mechanism in Organic Chemistry* (New York: Wiley, 1986)
100. F N Kaputskii, I A Bashmakov, E V Gert, A P Bobrovskii *Zh. Prikl. Khim.* **49** 2476 (1976)[a]
101. F N Kaputskii, A P Bobrovskii, E V Gert, I A Bashmakov *Zh. Prikl. Khim.* **52** 900 (1979)[a]
102. A P Bobrovskii, E V Gert, in *Soveshchanie "Khimiya i Tekhnologiya Proizvodnykh Tsellyulozy" (Tez. Dokl.)* [Conference 'Chemistry and Technology of Cellulose Derivatives' (Abstracts of Reports)] (Vladimir: All-Union Synthetic Resins Research Institute, 1980) Part I, p. 146
103. A P Bobrovskii, E V Gert, F N Kaputskii *Vestn. Belorus. Univ., Ser. 2* (1) 22 (1980)
104. USSR P. 802 286; *Byull. Izobret.* (5) 87 (1981)
105. A P Bobrovskii, E V Gert, A P Filanchuk, I A Bashmakov, F N Kaputskii *Vestn. Belorus. Univ., Ser. 2* (1) 12 (1981)
106. M V Shishonok, I A Bashmakov, E V Gert, F N Kaputskii *Khim. Drevesiny* (1) 20 (1988)
107. E L Akim, L P Perepechkin *Tsellyuloza dlya Atsetilirovaniya i Atsetaty Tsellyulozy* (Cellulose for Acetylation and Cellulose Acetates) (Moscow: Lesnaya Prom., 1971)
108. N I Klenkova *Struktura i Reaktsionnaya Sposobnost' Tsellyulozy* (The Structure and Reactivity of Cellulose) (Leningrad: Nauka, 1976)
109. G A Petropavlovskii, N E Kotel'nikova, L A Volkova *Cellul. Chem. Technol.* **16** 247 (1982)
110. E V Gert, M V Shishonok, F N Kaputskii, in *Soveshchanie "Khimiya i Tekhnologiya Proizvodnykh Tsellyulozy" (Tez. Dokl.)* [Conference 'Chemistry and Technology of Cellulose Derivatives' (Abstracts of Reports)] (Vladimir: The All-Union Research Institute of Synthetic Resins, 1980) Part II, p. 56
111. M V Makarenko, E V Gert, F N Kaputskii *Zh. Prikl. Khim.* **55** 2542 (1982)[a]
112. E V Gert, A Sokarras Morales, F N Kaputskii, in *Fizicheskie i Piziko-Khimicheskie Aspekty Aktivatsii Tsellyulozy (Tez. Dokl.)* [Physical and Physicochemical Aspects of the Activation of Cellulose (Abstracts of Reports)] (Riga: Zinatne, 1981) p. 126
113. A Sokarras Morales, A P Bobrovskii, E V Gert, F N Kaputskii *Zh. Prikl. Khim.* **55** 2364 (1982)[a]
114. F N Kaputskii, E V Gert, A P Bobrovskii, M V Shishonok *Zh. Prikl. Khim.* **53** 901 (1980)[a]
115. A Sokarras Morales, E V Gert, A P Bobrovskii, I A Bashmakov, F N Kaputskii *Vestn. Belorus. Univ., Ser. 2* (2) 11 (1982)

116. I A Bashmakov, E V Gert, F N Kaputskii, in *II Vsesoyuz. Simp. po Primeneniyu Kalorimetrii v Adsorbtsii i Katalize (Tez. Dokl.)* [The Second All-Union Conference on the Application of Calorimetry in Adsorption and Catalysis (Abstracts of Reports)] (Novosibirsk: Institute of Catalysis, Siberian Branch of the Academy of Sciences of the USSR, 1983) p. 29
117. A P Bobrovskii, I A Bashmakov, E V Gert, F N Kaputskii *Izv. Vysch. Uchebn. Zaved., Khim. Khim. Tekhnol.* **26** 364 (1983)
118. USSR P. 1 125 218; *Byull. Izobret.* (43) 69 (1984)
119. M V Shishonok, E V Gert, I A Bashmakov, F N Kaputskii *Izv. Akad. Nauk Belorus. SSR* (1) 28 (1989)
120. F N Kaputskii, N G Tsygankova, R G Zhbankov, D D Grinshpan, D K Buslov, in *Fizicheskie i Piziko-Khimicheskie Aspekty Aktivatsii Tsellyulozy (Tez. Dokl.)* [Physical and Physico-chemical Aspects of the Activation of Cellulose (Abstracts of Reports)] (Riga: Zinatne, 1981) p. 119
121. E V Gert, A Sokarras Morales, M V Makarenko, F N Kaputskii *Khim. Drevesiny* (3) 13 (1983)
122. E V Gert, A Sokarras Morales, M V Makarenko, in *V Vsesoyuz. Konf. po Khimii i Fizike Tsellyulozy. I. Fizika i Fiziko-Khimiya Tsellyulozy (Tez. Dokl.)* [The Fifth All-Union Conference on the Chemistry and Physics of Cellulose. I. The Physics and Physical Chemistry of Cellulose (Abstracts of Reports)] (Tashkent: Fan, 1982) p. 122
123. E V Gert, M V Shishonok, V I Torgashov, F N Kaputskii *Khim. Drevesiny* (5) 52 (1988)
124. E V Gert, A Sokarras Morales, M V Makarenko, F N Kaputskii *Khim. Drevesiny* (3) 19 (1983)
125. E V Gert, A Sokarras Morales, M V Makarenko, I A Bashmakov, in *V Vsesoyuz. Konf. po Khimii i Fizike Tsellyulozy. I. Fizika i Fiziko-Khimiya Tsellyulozy (Tez. Dokl.)* [The Fifth All-Union Conference on the Chemistry and Physics of Cellulose. I. The Physics and Physical Chemistry of Cellulose (Abstracts of Reports)] (Tashkent: Fan, 1982) p. 120
126. A Sokarras Morales, Candidate Thesis in Chemical Sciences, Belorussian State University, Minsk, 1982
127. A Sh Goikhman, V P Solomko *Vysokomolekulyarnye Soedineniya Vklyucheniya* (High-Molecular-Weight Clathrate Compounds) (Kiev: Naukova Dumka, 1982)
128. E V Gert, V I Torgashov, M V Shishonok, F N Kaputskii *Vysokomol. Soedin., Ser. A* **31** 1668 (1989)[b]
129. E V Gert, V I Torgashov, M V Shishonok, S I Sinyak, F N Kaputskii *J. Polym. Sci., Part B, Polym. Phys.* **31** 567 (1993)
130. A Sueoka, J Hayachi, S Watanabe *Nippon Kagaku Kaishi* **3** 594 (1973)
131. K Gess *Die Chemi der Zellulose und ihrer Begleiter* (Leipzig: Akademic-Verlag, 1928)
132. H Mark *Physik und Chemie der Cellulose* (Berlin: Springer, 1932)
133. V G Tsvetkov, N I Naimark, L Ya Tsvetkova, O A Zueva *Zh. Prikl. Khim.* **57** 1813 (1984)[a]
134. V I Torgashov, E V Gert, M V Shishonok, F N Kaputskii, in *Metody Issledovaniya Tsellyulozy (Tez. Dokl. Nauchn. Seminara)* [Methods for the Investigation of Cellulose (Abstracts of Reports at a Scientific Seminar)] (Riga: Institute of the Chemistry of Wood, Academy of Sciences of the Latv. SSR, 1988) p. 27
135. M V Shishonok, E V Gert, F N Kaputskii *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **30** 96 (1987)
136. E V Gert, M V Shishonok, V I Torgashov, F N Kaputskii *Dokl. Akad. Nauk Belorus. SSR* **32** 627 (1988)[f]
137. E V Gert, M V Shishonok, T I Filanchuk, V I Torgashov, O V Zubets, in *Vsesoyuz. Konf. "Khimiya, Tekhnologiya, Primenenie Tsellyulozy i ee Proizvodnykh", Cherkassy (Tez. Dokl.)* [All-Union Conference 'Chemistry, Technology, and Applications of Cellulose and Its Derivatives', Cherkassy (Abstracts of Reports)] (Vladimir: All-Union Synthetic Resins Research Institute, 1985) p. 59
138. E V Gert, M V Shishonok, V I Torgashov, F N Kaputskii *J. Polym. Sci., Part C, Polym. Lett.*, **28** 163 (1990)
139. USSR P. 1 328 349; *Byull. Izobret.* (29)113 (1987)
140. V I Torgashov, E V Gert, F N Kaputskii, in *Tez. Dokl. VI Vsesoyuz. Konf. po Fizike i Khimii Tsellyulozy* (Abstracts of Reports at the Sixth All-Union Conference on the Physics and Chemistry of Cellulose) (Minsk: Institute of Physics, Academy of Sciences of the Belorus. SSR, 1990) p. 267
141. S Watanabe, K Imai, J Hayachi *Koguo Kagaku Zasshi* **74** 1427 (1971)
142. A Sueoka, J Hayachi, S Watanabe *Nippon Kagaku Kaishi* **7** 1345 (1975)
143. USSR P. 1 244 151; *Byull. Izobret.* (26) 109 (1986)
144. USSR P. 1 381 118; *Byull. Izobret.* (10) 97 (1988)
145. V I Torgashov, E V Gert, A V Bil'dyukevich, F N Kaputskii *Dokl. Akad. Nauk Belorus. SSR* **33** 1017 (1989)
146. E V Gert, V I Torgashov, M V Shishonok, in *Vsesoyuz. Konf. "Khimiya i Reaktsionnaya Sposobnost' Tsellyulozy i ee Proizvodnykh" (Tez. Dokl.)* [All-Union Conference 'Chemistry and Reactivity of Cellulose and Its Derivatives (Abstracts of Reports)] (Frunze: Institute of Organic Chemistry, Academy of Sciences of the Kirg. SSR, 1991) p. 181
147. L I Batura, G A Vikhoreva, R M Noreika *Cellul. Chem. Technol.* **15** 487 (1981)
148. V I Torgashov, A V Bil'dyukevich, E V Gert, F N Kaputskii, in *Tez. Dokl. II Vsesoyuz. Konf. po Mikrobnym Polisakharidam* (Abstracts of Reports at the Second All-Union Conference on Microbial Polysaccharides) (Leningrad: Leningrad Chemical Pharmaceutical Institute, 1984) p. 59
149. V I Torgashov, E V Gert, V I Tyurin, in *Tez. Dokl. Vsesoyuz. Konf. "Problemy Ispol'zovaniya Tsellyulozy i ee Proizvodnykh v Meditsinskoi i Mikrobiologicheskoi Promyshlennosti", Moscow* (Abstracts of Reports at the All-Union Conference 'Problems of the Use of Cellulose and Its Derivatives in the Medical and Microbiological Industry', Moscow) (Tashkent: Institute of the Chemistry and Technology of Cotton Cellulose, 1989) p. 54
150. USSR P. 1 035 030; *Byull. Izobret.* (30) 73 (1983)
151. V Ya Bytenskii, E P Kuznetsova *Proizvodstvo Efirov Tsellyulozy* (Production of Cellulose Esters) (Leningrad: Khimiya, 1974)
152. USSR P. 491 650; *Byull. Izobret.* (42) 65 (1975)
153. Z B Komarova, V M Aver'yanova, O G Efremova, R Kh Kaibusheva *Khim. Volokna* (4) 31 (1979)
154. M V Shishonok, E V Gert, O V Zubets, in *Tez. Dokl. VI Vsesoyuz. Konf. po Fizike i Khimii Tsellyulozy* (Abstracts of Reports at the Sixth All-Union Conference on the Physics and Chemistry of Cellulose) (Minsk: Institute of Physics, Academy of Sciences of the Belorus. SSR, 1990) p. 174
155. O V Zubets, M V Shishonok, E V Gert, F N Kaputskii *Vestn. Belorus. Univ., Ser. 2* (2) 13 (1992)
156. E V Gert, M V Shishonok, O V Zubets, F N Kaputskii, in *Tez. Dokl. Vsesoyuz. Nauch. Konf. "Problemy Modifikatsii Prirodnykh i Sinteticheskikh Voloknoobrazuyushchikh Polimerov"* (Abstracts of Reports at the All-Union Scientific Conference 'Problems of the Modification of Natural and Synthetic Fibre Forming Polymers' (Moscow: Kosygin Moscow Textile Institute, 1991) p. 41
157. E V Gert, M V Shishonok, O V Zubets, F N Kaputskii, in *Tez. Dokl. XV Mendeleevskogo S'ezda po Obshchei i Prikladnoi Khimii, Minsk, 1993* (Abstracts of Reports at the XVth Mendeleev Congress on General and Applied Chemistry, Minsk, 1993) Vol. I p. 239
158. M V Shishonok, E V Gert, O V Zubets, A A Kuz'michev, L A Kuz'menkov *Vestn. Belorus. Univ., Ser. 2* (2) 10 (1988)
159. E V Gert, M V Shishonok, O V Zubets, F N Kaputskii, in *Tez. Dokl. VI Vsesoyuz. Konf. po Fizike i Khimii Tsellyulozy* (Abstracts of Reports at the Sixth All-Union Conference on the Physics and Chemistry of Cellulose) (Minsk: Institute of Physics, Academy of Sciences of Belorus. SSR, 1990) p. 175
160. E V Gert, M V Shishonok, O V Zubets, V I Torgashov, F N Kaputskii *Vysokomol. Soedin., Ser.* **37A** 1130 (1995)[b]

[a] — *Russ. Appl. Chem. (Engl. Transl.)*
[b] — *Russ. Polym. Sci. (Engl. Transl.)*
[c] — *Pharm. Chem. J. (Engl. Transl.)*
[d] — *Russ. J. Gen. Chem. (Engl. Transl.)*
[e] — *Russ. Crystallogr. (Engl. Transl.)*
[f] — *Dokl. Chem. (Engl. Transl.)*