

# A Study of the Low Temperature Nitration of Cellulose in Mixed Acids

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## Synopsis

The low temperature surface and bulk nitration of cellulose has been investigated by electron spectroscopy for chemical analysis (ESCA),  $^{13}\text{C}$ -NMR and X-ray diffraction. Acid mix composition has been probed at room temperature and at low temperatures (0–20°C) by Raman spectroscopy. This multitechnique approach has been employed to elucidate the behavior of surface degree of substitution (DOS) with acid mix composition over a 40°C temperature range. The data obtained have prompted a reinterpretation of previously reported work. Surface "equilibrium DOS" is shown to be established within 1 s at all temperatures investigated, but, at lower temperatures (< 5°C) the surface DOS as monitored by ESCA is observed to "dip" after immersion times of  $t > 5$  s. This change in DOS is correlated with major structural changes in the fiber as observed by SEM. At low temperatures, e.g., -15°C, nitration is shown to be complete throughout the cellulose fiber after 10 h nitration. Solution state  $^{13}\text{C}$ -NMR is used to compare the nitrate ester substitution distribution in cellulose nitrates prepared from acid mixes of the same composition at different temperatures.

## INTRODUCTION

At room temperature the nitration of cellulose in technical acid mixes at the surface region is extremely rapid; the equilibrium DOS is established to a depth of  $> 100$  Å in about 1 s. Hence in practice it has proved impossible to study the approach to equilibrium DOS as a function of time, at room temperature, as the nitration and quenching procedures cannot be carried out in much less than a second.<sup>1</sup>

In an attempt to slow down the initial stages of reaction at the cellulose surface of Whatman no. 1 papers, Clark et al.<sup>2,3</sup> carried out nitrations in a technical acid mix at reduced temperatures for 30 s. The nitrated samples were analyzed by ESCA ( $\text{Mg}_{\text{K}\alpha}$  X-rays) and the surface DOS calculated from the  $\text{N}_{1s}$  and  $\text{C}_{1s}$  core level area ratios.<sup>1</sup> The surface DOS achieved was reported to be temperature dependent; at temperatures above 5°C the DOS was not observed to be affected by temperature; between 5°C and -15°C DOS decreased with acid mix temperature; below -15°C DOS did not further decrease with nitration temperature. Fowler<sup>4</sup> repeated the experiment em-

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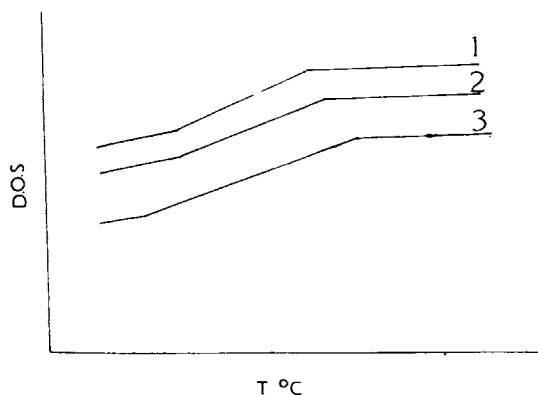


Fig. 1. Schematic of surface DOS vs. nitration temperature: (1) 75%  $\text{H}_2\text{SO}_4$ , 22.5%  $\text{HNO}_3$ , 2.5%  $\text{H}_2\text{O}$ ; (2) 70%  $\text{H}_2\text{SO}_4$ , 22.5%  $\text{HNO}_3$ , 7.5%  $\text{H}_2\text{O}$ ; (3) 65%  $\text{H}_2\text{SO}_4$ , 22.5%  $\text{HNO}_3$ , 12.5%  $\text{H}_2\text{O}$ .

employing three technical acid mixes,

(1)	75% $\text{H}_2\text{SO}_4$ ,	22.5% $\text{HNO}_3$ ,	2.5% $\text{H}_2\text{O}$
(2)	70% $\text{H}_2\text{SO}_4$ ,	22.5% $\text{HNO}_3$ ,	7.5% $\text{H}_2\text{O}$
(3)	60% $\text{H}_2\text{SO}_4$ ,	22.5% $\text{HNO}_3$ ,	17.5% $\text{H}_2\text{O}$

and three temperature vs. DOS curves were produced, shown schematically in Figure 1. From this figure it can be seen that the three curves are parallel to each other. Three possible explanations have been forwarded to describe the shape of these curves.<sup>4</sup> They are:

- (i) a possible kinetic effect, where the nitration reaction is slowed down by reduction in acid mix temperature
- (ii) inhomogeneous nitration in the surface after 30 s
- (iii) a possible thermodynamic effect, where the nitration-denitration equilibrium is perturbed in favour of denitration at lower temperature

The first explanation, inhomogeneous nitration over the top 50 Å ( $\text{Mg}_{K\alpha}$  sampling depth), was discounted on the grounds that the DOS as monitored by  $\text{Ti}_{K\alpha}$  X-rays (sampling depth typically 100 Å) was essentially the same as that at 50 Å.

To ascertain the possible role of kinetics in the nitration reaction, the immersion time at  $-25^\circ\text{C}$  was extended to 1 h; after 1 h nitration the surface DOS was unchanged and further no bulk nitration could be detected.

Hence, it was suggested<sup>4</sup> that the effect of lowering the nitration temperature is to perturb the thermodynamics, rather than the kinetics, of nitration. The DOS values obtained were, therefore, taken to be representative of "final equilibrium" DOS and the linear portions of the three curves were treated employing the van 't Hoff Isochore<sup>5</sup> to determine the enthalpy of reaction ( $H^0$ ) in each of the three mixes; the activities of the acids and water were taken to be unity, and temperature independent, and the DOS was treated as the activity or concentration of the product at the various temperatures.  $\Delta H^0$

was calculated to be endothermic in the three acid mixes investigated. In contrast, from microcalorimetric studies of nitration Calvets<sup>6</sup> determined the heat of formation to be  $-20$  kcal/mol, i.e., exothermic, for cellulose nitrates of 11.7–13.0% N.

In previous publications it has been shown that the surface DOS achieved in a cellulose, by nitration with a technical mixed acid, is controlled by competing nitration–denitration reactions.<sup>7,8</sup> At room temperature an acid mix capable of only supporting a 2.0 DOS cellulose nitrate will denitrate a higher DOS material.<sup>9</sup> In the cellulose bulk denitration is slow, since the diffusion of the acid mix into the fibers is slow. However, at the fiber surface ESCA has shown denitration to be extremely rapid.<sup>1</sup> From Figure 1 it is evident that the surface DOS achieved by nitration in acid mixes maintained at lower temperatures is considerably reduced from that achieved by nitrating in the same mixes when maintained at typical room temperatures (16–22°C). If the lowering in DOS, with temperature, is a consequence of a perturbation in the nitration–denitration equilibria, then it would be expected that at lower temperatures a technical acid mix will no longer support the cellulose nitrate manufactured in that mix at room temperature. Employing ESCA it is possible to monitor any potential denitration at the fiber surface resulting from a reimmersion of a cellulose nitrate back in its own nitrating mix maintained at low temperature.

In this paper ESCA is employed to monitor the action of technical mixed acids over the temperature range  $-25^{\circ}\text{C}$  to  $+22^{\circ}\text{C}$  at the surfaces of cellulose and cellulose nitrates; Raman spectroscopy is utilized to examine the effect of temperature on the concentration of the various species in technical acid mixes.  $^{13}\text{C}$ -NMR is employed to investigate the nitrate ester substitution distribution obtained in cellulose nitrate prepared at different temperatures.<sup>9</sup>

## EXPERIMENTAL

The cellulose nitrates used in this work were prepared from cellulose Whatman no. 1 papers or from cellophane sheets supplied by British Cellophane Ltd. The cellophane sheets were prepared by the viscose process. The sheets were without additives; the major impurities were sodium ( $< 10$  ppm), chlorine ( $< 10$  ppm) and sulfur (50 ppm). The papers and cellophane were predried in a vacuum oven for 2 h at  $60^{\circ}\text{C}$  and then stored over  $\text{P}_2\text{O}_5$  until nitration. This provides a cellulose of  $< 2\%$  water.<sup>1</sup> Nitration was accomplished by the immersion of the cellulose material in the appropriate acid mixes as depicted in Figure 2. An acid/cellulose ratio of approximately 100 : 1 was employed. Nitration was quenched by plunging the cellulose into 1 L of rapidly stirred iced water. This quenching procedure has been shown to minimize possible denitration which can occur with dilution of the acid mix.<sup>10</sup>

Nitrations at low temperature were accomplished by either cooling the acid mix in a freezer or by means of a acetone/dry ice slush bath ( $-20^{\circ}\text{C} \leftrightarrow 0^{\circ}\text{C}$ ).

Solution state  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker AC 250 spectrometer, proton noise decoupled (62 MHz) with typical acquisition times of 9–12 h.

ESCA spectra were run on a Kratos ES300 electron spectrometer employing  $\text{Mg}_{K\alpha}$  X-rays. Peak fitting was achieved using the software on a Kratos

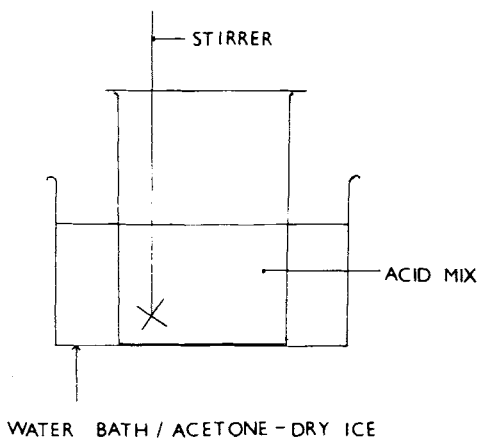


Fig. 2. The nitrating apparatus.

DS300 data system. DOS was calculated from the  $N_{1s}$  and  $C_{1s}$  core level area ratios.<sup>1</sup>

All Raman spectra were run on a Varian Cary 82 Raman spectrophotometer using an argon gas laser (514.5 nm, 200 mW). The temperature of the acid mix monitored was regulated by means of a liquid nitrogen cooled cryostat.

## RESULTS AND DISCUSSION

### A Study of "Low Temperature Denitration"

A cellulose nitrate of surface DOS 2.3 was prepared in a 75%  $H_2SO_4$ , 22.5%  $HNO_3$ , 2.5%  $H_2O$  technical acid mix at room temperature. Pieces of this cellulose nitrate were immersed in fresh acid mixes of the same composition for  $> 2$  min at various temperatures in the range  $+20$ – $-20^\circ C$ . The surface DOS of the reimmersed materials was monitored by ESCA and the results are displayed in Table I.

From the table it can be seen that the original surface DOS of the starting cellulose (2.3) remains unaffected by the immersions. Further, extending the immersion time produced no change in DOS.

However, when cellulose papers (Whatman no. 1) were nitrated in a 75%  $H_2SO_4$ , 22.5%  $HNO_3$ , 2.5%  $H_2O$  acid mix for 2 min at  $-15^\circ C$ , the resulting DOS achieved was about 1.4.

TABLE I  
Surface DOS with Acid Mix Temperature

Temperature of acid mix	Degree of substitution
20°C	2.3
- 7°C	2.4
-15°C	2.3
-20°C	2.3

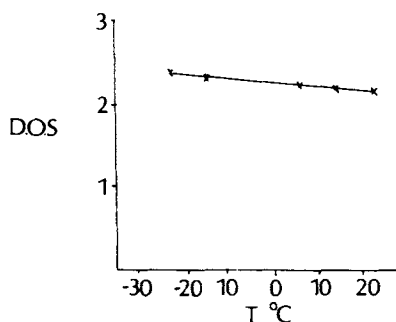


Fig. 3. Denitration of 2.6 DOS cellulose nitrate: DOS vs. denitration temperature.

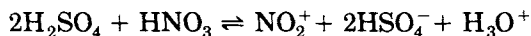
It was suggested in the Introduction that denitration would be expected from the reimmersion of a cellulose nitrate back into a technical acid mix maintained below 5°C. This expectation was based on the premise that the nitration–denitration equilibria are perturbed in favor of denitration at low temperature. However, the above result shows that this is evidently not the case.

It is important to note that the denitration reaction is still observed in technical acid mixes maintained at low temperature. Pieces of a cellulose nitrate, surface DOS 2.6, immersed in an acid mix that supports a surface DOS of 2.2 at room temperature for 30 s at various temperatures in the range –25–+20°C, showed appreciable surface denitration (see Fig. 3). The slightly greater DOS observed at lower temperatures is thought to be significant, indicating that the nitration–denitration equilibrium is perturbed in favor of nitration at lower temperatures. This result is consistent with the nitration reaction being exothermic as reported by Calvets.<sup>6</sup> This conclusion is in direct contrast to the conclusion drawn from previously reported data.<sup>4</sup>

The difference in the DOS obtained from nitration (2 min) and denitration at low temperature clearly does not fit well with an equilibrium view of the nitration reaction. If the DOS obtained is equilibrium controlled, at low temperature, then the DOS obtained by nitration and denitration ought to be the same.

### A Raman Temperature Study of Mixed Acids

The importance of the balance position of the equilibrium,



in determining the final surface DOS achieved in the nitration of cellulose with technical mixed acids is well established.<sup>7,8</sup> By monitoring the relative concentration of the above species in technical mixed acids, changes in the surface DOS have been rationalized.<sup>8</sup> Employing Raman spectroscopy, the relative concentrations of the above species can be monitored in a particular acid mix over a range of temperatures.

Raman scans 250–1500 cm<sup>-1</sup> of a 75% H<sub>2</sub>SO<sub>4</sub>, 22.5% HNO<sub>3</sub>, 2.5% H<sub>2</sub>O acid mix were recorded at +20, +3, and –19°C (see Fig. 4). The band assignments

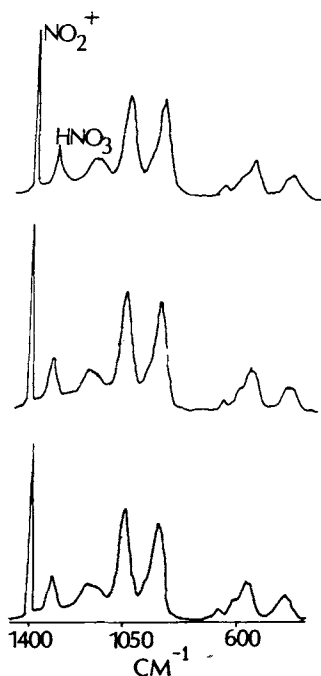


Fig. 4. Raman spectrum of technical acid mix at three different temperatures.

in this Figure were made on the basis of those described by Ingold.<sup>11</sup> From comparison of the peak heights at 1400 and 1300  $\text{cm}^{-1}$  the concentration of the nitronium ion relative to that of molecular nitric acid can be compared; from Figure 4 it can be seen that the relative concentration of these two species is independent of temperature.

The Raman scans of a 67%  $\text{H}_2\text{SO}_4$ , 25%  $\text{HNO}_3$ , 8%  $\text{H}_2\text{O}$  acid mix were recorded  $-20$  and  $+20^\circ\text{C}$ . Again, the concentration of nitronium ion relative to that of nitric acid in this mix remains essentially independent of temperature.

It has been proposed<sup>4</sup> that the DOS, monitored by ESCA after 30 s nitration, at different temperatures in the range  $+25$ – $-20^\circ\text{C}$  represented "final equilibrium" surface DOS. It was considered either "that the equilibrium constant for the formation of the nitrating species [now established as the nitronium ion]" or "that the equilibrium constant for the reaction of the nitrating agent with the hydroxyl groups" are temperature dependent. From the Raman study it is evident that the equilibrium describing the formation of the nitrating agent, the nitronium ion, is not temperature-sensitive. If the formation of the nitrating species is the predominant factor controlling the DOS obtained in mixed acids, then no significant change in surface DOS would be anticipated as the temperature of the nitrating acid mix is reduced. This conclusion fits well the data presented in Table I and Figure 3.

It is still possible that the equilibrium constant for the reaction of the nitronium ion with the cellulose hydroxyls is temperature-dependent. However, this hypothesis fails to explain why a technical acid mix, maintained at

low temperature, although capable of denitration continues to support a cellulose nitrate of a high DOS.

In view of the conflict in our own data and the data previously reported,<sup>2,4</sup> it was decided to experimentally reinvestigate low temperature nitration.

### Low Temperature Nitration

Cellulose papers were immersed in a 60% H<sub>2</sub>SO<sub>4</sub>, 25% HNO<sub>3</sub>, 15% H<sub>2</sub>O technical mixed acid maintained at about -15°C for 3 h. The papers were then analyzed by ESCA and by micro-Kjeldahl analysis. Two important observations were made:

- (i) The "final" surface DOS was found to be 2.4
- (ii) The bulk nitrogen content of the cellulose nitrate was > 12% by weight, after washing and appropriate stabilization

These results were not expected as they are in direct contrast to results previously reported<sup>2,4</sup> where extended immersion times did not result in an increased surface DOS or bulk nitration. It was therefore considered important to examine both the surface and bulk nitration of cellulose as a function of time.

### The Bulk Nitration of Cellulose with Technical Mixed Acids Maintained at Low Temperature

Cellulose papers were nitrated in a technical mixed acid of the composition 75% H<sub>2</sub>SO<sub>4</sub>, 22.5% HNO<sub>3</sub>, 2.5% H<sub>2</sub>O at +22 and at -15°C. At -15°C the acid mix was very viscous, and hence nitration in the bulk of the cellulose was found to proceed very slowly. Complete penetration of the cellulose fibers by the acid mix was determined by the solubility of the nitrated product in d<sub>6</sub>-dmsO.<sup>10</sup> Cellulose nitrates of a DOS < 1.8 are insoluble in this reagent; incomplete penetration of the cellulose fiber by an acid mix will result in regions where the DOS is < 1.8 and hence the fiber will not be completely soluble in d<sub>6</sub>-dmsO. Typical nitration times of about 10 h were found to be necessary to facilitate even nitration throughout the cellulose papers. In Table II the maximum surface and bulk DOS achieved by nitration at room temperature and low temperature (-15°C) are compared.

From this table it can be seen that the surface DOS of the two materials are comparable and that the bulk DOS of the two materials are comparable, although the surface and bulk DOS for each individual cellulose nitrate are

TABLE II  
DOS from Nitration at +22 and -15°C

Nitration temperature	DOS	
	surface	bulk
22°C	2.35	2.8
-15°C	2.45	2.8

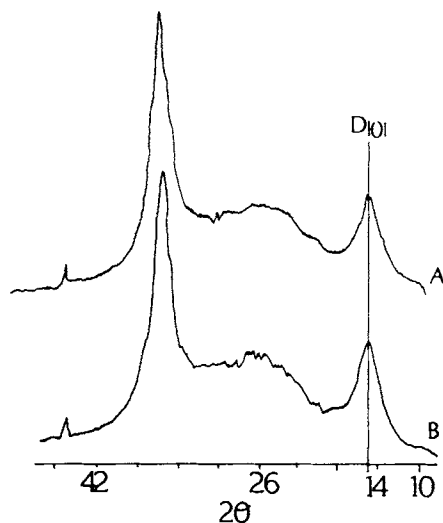


Fig. 5. X-ray diffractogram of cellulose nitrates prepared at (A) 22°C and (B) -15°C.

not the same; a full explanation for this will be presented in a future publication.<sup>12</sup>

The use of X-ray diffraction to investigate the crystal structure of cellulose nitrate has been reviewed by Miles.<sup>13</sup> Briefly, there exists a correlation between the angle of scattering  $\theta$  from the  $d_{101}$  plane and the %N of the cellulose nitrate; it has been observed that the  $d_{101}$  spacing increases with an increasing %N in the cellulose nitrate.<sup>14,15</sup> X-ray diffraction scans from  $4^\circ$  in  $2\theta$  to  $30^\circ$  in  $2\theta$  for the two materials are displayed in Figure 5. From this figure it can be seen that the  $d_{101}$  spacings in the two cellulose nitrates are the same.

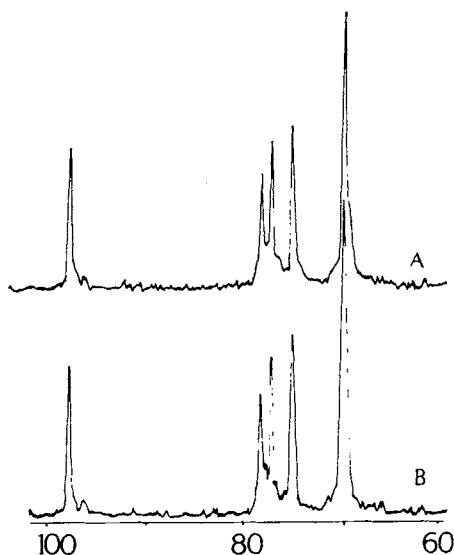


Fig. 6. <sup>13</sup>C-NMR spectra of cellulose nitrates prepared at (A) 22°C and (B) -15°C.



Solution state  $^{13}\text{C}$ -NMR has been shown to be a powerful tool for elucidating the substitution distribution of nitrate groups in the anhydroglucose residues.<sup>9</sup> Analysis of the complete solution state NMR spectrum has been described by Clark et al.<sup>16</sup>

The solution state  $^{13}\text{C}$ -NMR spectra of the two cellulose nitrates (Table II) were recorded and the resulting spectra are displayed in Figure 6. From visual examination of the spectra it is clear that the nitrate ester functionalities are similarly distributed in the two cellulose nitrates. In other cellulose nitrates of lower DOS, the substitution distribution patterns were also observed to be the same, i.e., substitution distribution is independent of the nitration temperature. However, it is important to point out that materials of similar DOS do not always display the same substitution distribution pattern.<sup>17</sup> Cellulose nitrates prepared from dichloromethane/nitric acid mixes display very different substitution distribution patterns to their mixed acid prepared counterparts at equivalent DOS.<sup>17</sup>

Hence, from the X-ray diffractograms and the  $^{13}\text{C}$ -NMR spectra it is evident that cellulose nitrates prepared at room temperature and at  $-15^\circ\text{C}$  are very similar in bulk structure.

#### Surface Nitration in Mixed Acids at Low Temperature as a Function of Time

In technical mixed acids, at room temperature, the equilibrium DOS is established in the surface region to a depth of at least 100 Å in the first second of immersion. The rate of nitration in mixed acids maintained at low temperatures does not, from the work reported above, appear to be as rapid. However, it has been shown that the schematics (Fig. 1) are not representative of the equilibrium DOS. To gain a better understanding of the processes taking place at the cellulose surface that might have produced these curves, ESCA was employed to follow the surface nitration of cellulose papers with time: nitrations in a 75%  $\text{H}_2\text{SO}_4$ , 22.5%  $\text{HNO}_3$ , 2.5%  $\text{H}_2\text{O}$  technical mixed acid were carried out at  $-15^\circ\text{C}$ . The results are displayed in Table III.

From this table it can be seen that nitration in the surface region is extremely rapid, at  $t < 5$  s the surface DOS reached is comparable with the room temperature "equilibrium" value. However, the overall behavior of DOS with time is unexpected and initially seems to be incompatible with the laws

TABLE III  
Surface DOS with Time: Nitration at  $-15^\circ\text{C}$

Time (s)	DOS
< 5	2.00
10	1.80
20	1.50
120	0.96
240	0.95
300	1.21
1620	2.29
6540	2.32
10,200	2.36
2.5 days	2.28

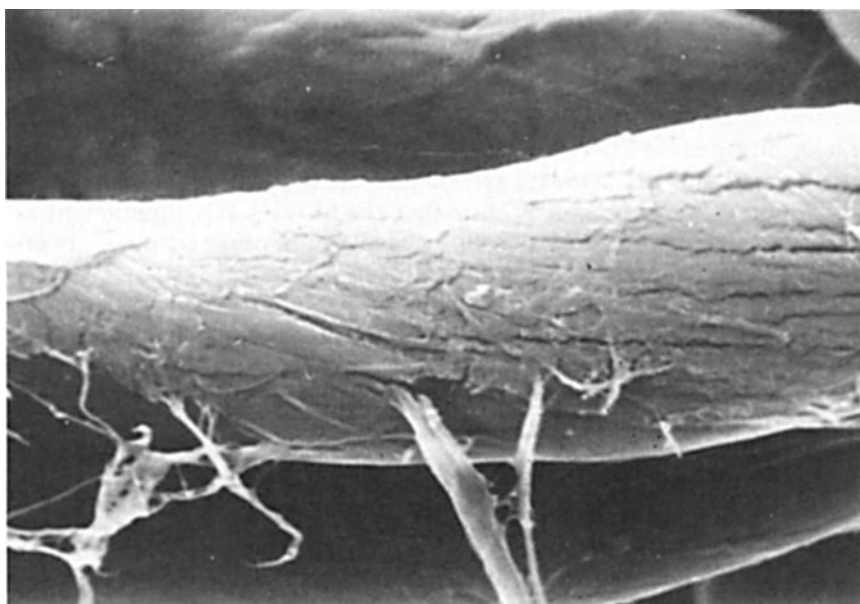


Fig. 7. SEM of cellulose fiber after 5 s nitration.

of mass action. The cellulose nitrates produced after immersion times of greater than 5 s were noticed to be extremely brittle and consequently very difficult to mount on a probe tip prior to analysis by ESCA. The brittleness is perhaps attributable to stresses imposed in the material by nitration limited to the surface of the fiber. X-ray diffraction studies<sup>14,15</sup> have shown that the dimensions of the unit cell of cellulose nitrate are larger than those of the cellulose unit cell: it is not unreasonable to assume that the accommodation of these two different unit cells in one material produces considerable stress, i.e., brittleness.

The DOS presented in Table III provide information on the level of nitration in, approximately, the top 50 Å of the cellulose. It is very unlikely that the "overall" level of nitration in the cellulose drops after 5 s immersion. However, it seems reasonable to assume that the cellulose fiber structure is undergoing considerable reorganization with nitration and ESCA is monitoring the effects of this "reorganization" in the fiber surface. Employing scanning electron microscopy (SEM) the surfaces of the cellulose fibers have been examined at two different nitration times (Figs. 7 and 8).

Visual examination of the micrographs presented reveals that a "cracking" in the fiber surface has occurred between  $t = 5$  s and  $t = 30$  s; i.e., destruction of the fiber surface is concomitant with nitration. It is envisaged that the fiber cracking results from stresses, imposed by nitration, in the cellulose surface. Fiber splitting will present a new cellulose surface to the nitrating mix; when the nitration is quenched immediately and the nitrating mix is washed away, the cellulose surface monitored by ESCA will consist of nitrated cellulose and the new unsubstituted cellulose surface. At  $t < 5$  s no cracking is observed in the SEM micrographs of the cellulose fibers. At  $t > 5$  s the onset of splitting occurs and the nitrated materials become brittle; the surface DOS, monitored by ESCA, drops.

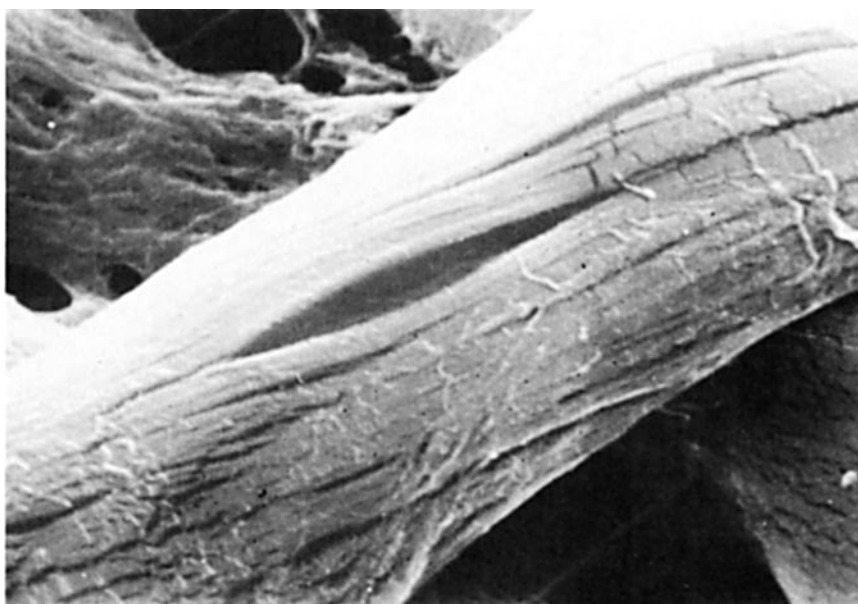


Fig. 8. SEM of cellulose fiber after 30 s nitration.

The severity of the observed cracking is most probably heightened by quenching when nitration is limited to the very surface and by the temperature gradient which exists between the nitrating mix,  $-15^{\circ}\text{C}$ , and the cellulose,  $+22^{\circ}\text{C}$ .

The cracking phenomenon reported is similar to that observed in cellophane at room temperature at the onset of nitration (see Figs. 9 and 10<sup>10</sup>). However, in cellophane the cracking is a lot more severe. Fully nitrated cellophanes are still extremely brittle. Above, the fully nitrated fibers were not at all brittle.

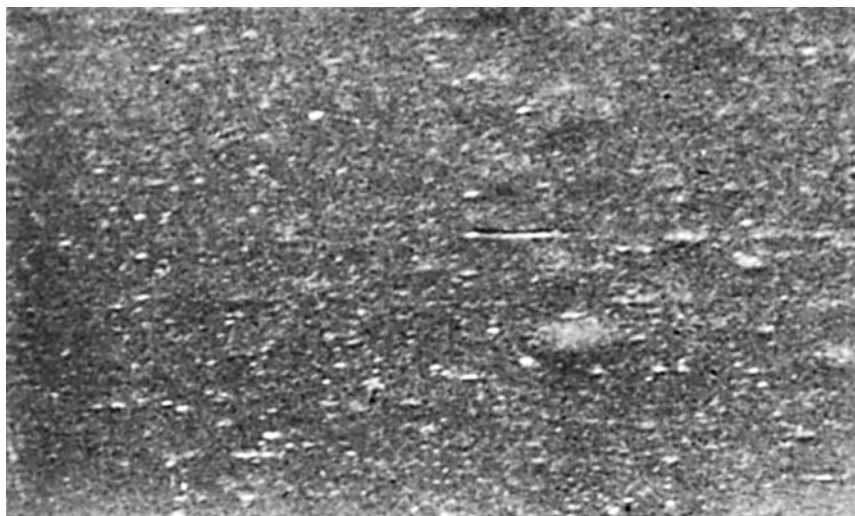


Fig. 9. SEM of cellophane sheet.

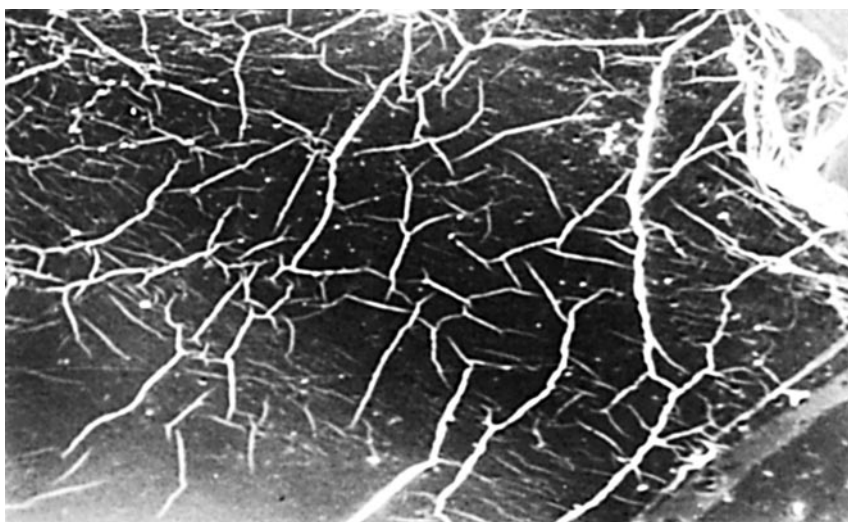


Fig. 10. SEM of cellophane sheet after 30 s nitration.

It is anticipated that, at room temperature, cracking must occur in the initial stages of nitration in cellulose fibers, but because the rate of diffusion of the acids into the cellulose subsurface is very much faster at room temperature than at reduced acid temperatures, the cracking is not severe.

The surface nitration of cellulose papers in a 75%  $\text{H}_2\text{SO}_4$ , 22.5%  $\text{HNO}_3$ , 2.5%  $\text{H}_2\text{O}$  acid mix has been monitored as a function of time and the results are presented in Table IV. The nitration reaction was quenched immediately. From Table IV it can be seen that the predicted dip in DOS can be observed at  $t = 15$  s but it is neither as dramatic nor as persistent as that observed in low temperature nitrations.

The cracking phenomenon has since been observed in different composition acid mixes and in other nitrating systems; it manifests as a dip in the DOS monitored by ESCA during the initial stages of nitration.<sup>10</sup> It is thought that fiber cracking at the onset of nitration is responsible for the form of the curves shown in Figure 1.

TABLE IV  
Surface DOS with Time: Nitration at +22°C

Time of nitration (s)	DOS
1	2.05
15	1.90
60	2.30
420	2.25
2400	2.38

## SUMMARY

In this paper it has been shown that the nitration–denitration equilibrium established between cellulose and mixed acids does not exhibit the previously reported temperature dependence. At low temperature, nitration in the surface region occurs on a similar time scale to nitration at room temperature. Bulk cellulose nitration at low temperatures requires much longer immersion times because of the increased viscosity of the acids. The DOS vs. temperature curves previously reported do not represent final DOS and are thought to be produced as a result of cracking in the fiber surface (reorganization of the fiber structure) with nitration.

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