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Experiments on the Effect of Ethylamine Treatment on the Crystallinity of Cellulose*

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Synopsis

The results of the effect of ethylamine treatment on the crystallinity of cellulose under various conditions have been presented. The mode of removal of the swelling agent from cellulose is important in determining the amount of change in the lateral order structure of cellulose. It seems that the apparent change in crystallinity observed by ethylamine treatment is due to the swelling of cellulose, producing disorder only in the so-called amorphous content of cellulose.

INTRODUCTION

The effect of ethylamine treatment on cellulose has been of considerable interest for many years and has been the subject of many investigations. Several years ago, Davis et al.[1] reported that cellulose is readily swollen by the lower primary amines, namely, methylamine, ethylamine, and propylamines, but that it must be preswollen with liquid ammonia before isopropylamine or any of the butylamines would produce a change in the x-ray diffractogram. Segal et al.[2] investigated the effect of ethylamine and hexylamine on cellulose and found that the crystallinity could be considerably reduced by this treatment. They also found that cotton, first treated with ethylamine and then with hexylamine overnight and then extracted with chloroform, showed 46% crystallinity. When this sample was boiled in water for 2 hr. no appreciable restoration in the crystallinity was observed. Sisson[3] and Kouris et al.[4] have shown that if the swelling agent is removed by a nonpolar solvent a lower value in crystallinity is observed. Further, investigations have shown that monoethylamine appears to be the most effective of various alkylamines in swelling cellulose. They found a reduction of 23% in viscosity for cotton when treated in air as against the viscosity of the original sample. In treating cellulose with anhydrous ethylamine the effect of treatment occurred in the first 15 min. although it took 4 hr. for complete reaction. In a later paper, Segal et al.[5] reported the results of a study of the decomposition of the ethylamine-cellulose complex

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obtained from cotton cellulose. It is reported that ethylamine-treated cellulose, when boiled in water for 2 hr., regenerates cellulose I.

Loeb and Segal[6] have shown that the extent of "reduction of crystallinity" could be controlled by using ethylamine of various concentrations in water. However, it is found that ethylamine of 71% or less concentration does not produce appreciable change in crystallinity. In other words, 70% or less ethylamine in water behaves similarly to water alone. Treatment of cellulose with ethylamine of 75–90% produces only a change of about 20% in crystallinity. This number is obtained by calculating the crystallinity index by Segal's formula from the x-ray diffractograms. This method of changing the crystallinity has been used for the studies of viscoelastic properties[7] and dielectric properties[8] of several cellulosic materials. It should be emphasized that in studying the crystallinity of cellulose the powder technique developed independently by Debye and Scherrer[9] is usually employed. It has been found that several factors influence this method of determining the crystallinity of cellulose.[10] Accordingly, in the present investigation, rectangular pieces of sheets cut from handsheets made in a British sheet mold have been used.

Recent investigations in this laboratory in which cellulose was treated with various concentrations of ethylamine have disclosed that if the treated samples are beaten the original crystallinity is restored.[10] X-ray diffractograms of ramie are given in Figures 1 and 2. Figure 1 shows a ramie sample which was degummed, bleached, and treated with 5% sodium hydroxide and then beaten for 50 min. in a Jokro mill. Figure 2 shows a ramie sample treated as in the first case but beaten for 50 min. after 99.8% ethylamine treatment. The change in height of the peaks is due to the difference in the mass of the material used.

It is seen that crystallinities of these two samples determined by Segal's formula are the same. Cotton linters also showed the same behavior. In view of these surprising preliminary results, a more thorough investigation of these phenomena was undertaken, and the results are reported in this paper.

EXPERIMENTAL

Treatment of Cellulose in Air and in Vacuum

It was mentioned earlier that beating a cellulose sample after treatment with ethylamine restored the original crystallinity. It is seen from the x-ray diffractograms reported by Loeb and Segal[6] that only a reduction of about 20% in crystallinity, as calculated by the Segal formula, takes place by treating cellulose with 90% ethylamine. Parker[7] treated pure cotton rags with 85 and 94% aqueous ethylamine and found the crystallinities to be 53.2 and 51.5%, respectively. From this it is seen that if cellulose is treated with ethylamine of concentration above 85% very little further decrease in crystallinity occurs. Kouris et al.[4] have reported that if a wet cellulose sample is freeze-dried from benzene after solvent exchange the

TABLE I
Results Obtained by Treatment of Cellulose With Ethylamine in Air and in Vacuum

Sample and Treatment	Viscosity, cp.[a]
Original cotton linters	48.4
Linters treated with anhydrous ethylamine in vacuum	45.3
Linters treated with anhydrous ethylamine in air	45.8
Linters beaten 140 min. in a Jokro mill	39.9
Linters beaten 140 min. in a Jokro mill followed by treatment with anhydrous ethylamine	38.3
Linters treated with anhydrous ethylamine followed by beating 140 min. in a Jokro mill	36.4

[a] Values are based on at least two duplicate viscosity runs.

crystallinity is reduced by about 8%. This decrease in crystallinity might be due to the fact that water is a swelling agent for cellulose and can produce a change in the amorphous content of cellulose. In the case of cellulose, either unbeaten or beaten, treatment with only ethylamine produces a change of about 20%. This also might be due to the fact that ethylamine is a more powerful swelling agent than water and, consequently, the change produced in the amorphous part of cellulose is greater So it is definitely not known whether the ethylamine with various percentages of water "decrystallizes" cellulose Thus, there is the possibility that the ethylamine merely produces increased disorder by swelling the so-called amorphous content of cellulose If this possibility holds, then if cellulose is treated in air, no degradation should take place. Accordingly, a cellulose sample was treated in vacuum and in air by the experimental procedures reported elsewhere.[8] The viscosities of the samples treated in air and vacuum were measured on the basis of the viscosity in cupriethylenediamine by the 1 g. concentration method of TAPPI T 230 sm-50. In addition to these experiments, the viscosities of the following samples were measured for cotton linters: (*1*) untreated; (*2*) vacuum treated with anhydrous ethylamine and then beaten 140 min. in a Jokro mill; (*3*) beaten 140 min. in a Jokro mill and then vacuum treated with anhydrous ethylamine; (*4*) beaten 140 min. in a Jokro mill. The results are given in Table I.

It will be seen from Table I that cellulose, if treated with ethylamine in air, is not degraded as reported earlier.[1] Table I also discloses that if cellulose after treatment is beaten, then a marked decrease in viscosity is observed of about 23%.

Influence of Beating Before and After Ethylamine Treatment

The influence of beating has been reported as mentioned above. The effect of this on ramie as well as on cotton linters is given in Figures 1–4. It is seen that samples beaten before ethylamine treatment retain the change in crystallinity due to ethylamine treatment, while samples beaten after ethylamine treatment regained the original crystallinity within experimental error. The following tentative statements are made to explain the

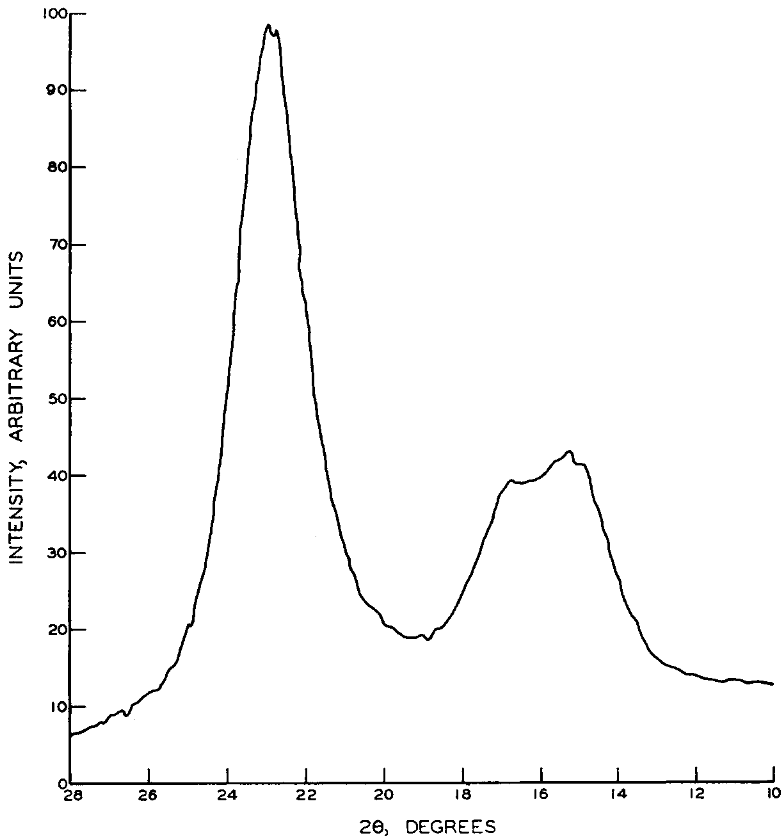

Fig. 1. X-ray diffractogram of ramie, degummed, bleached, treated with 5% sodium hydroxide, beaten for 50 min., and made into handsheet.

above observations. Ethylamine entering the microfibrils swells the disordered regions in cellulose, leaving the crystalline regions intact. It should be kept in mind that the total change taking place by this treatment is only about 20%. When this swelling effect due to ethylamine is removed by beating in a Jokro mill, the original crystallinity is restored. This is seen from Figure 2.

Extraction of Ethylamine by Chloroform

Segal and his co-workers reported[2] that if the amines from cellulose treated with ethylamine and kept overnight in hexylamine are removed in a Soxhlet with chloroform, and a few milliliters of 85% phosphoric acid are added, a low value of 46% crystallinity (acid hydrolysis method) could be obtained. The original crystallinity of the sample was reported to be 89%. Similar experiments were conducted in this laboratory in which cotton linters of 86% crystallinity were immersed in only ethylamine overnight and the amine removed by chloroform extraction as reported above.

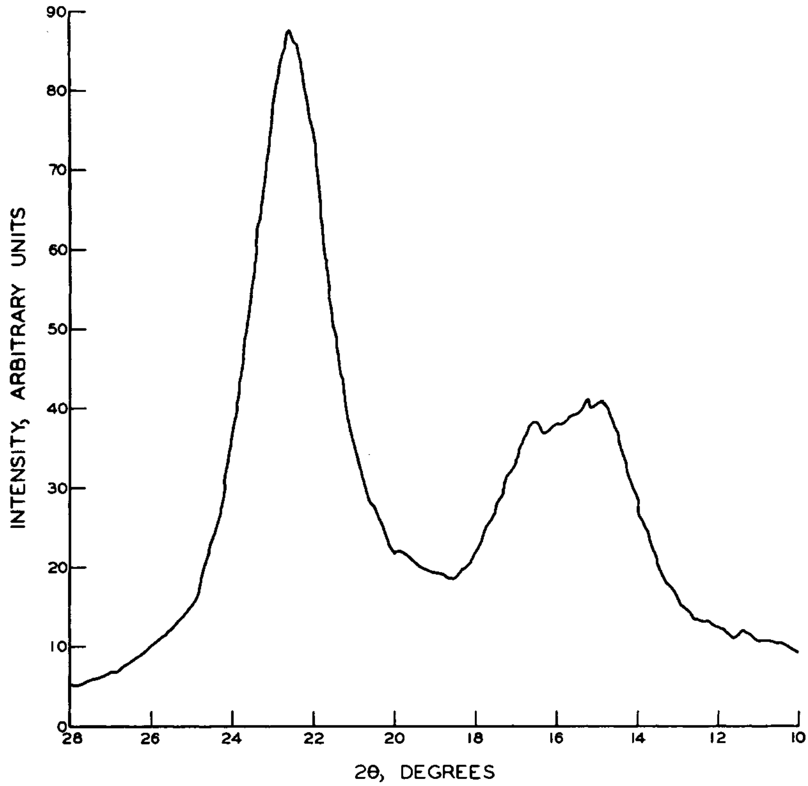

Fig. 2. X-ray diffractogram of ramie, degummed, bleached, treated with 5% sodium hydroxide, with 99.8% ethylamine, beaten for 50 min., and made into handsheet.

The crystallinity index was found to be 75%. The diffractogram is shown in Figure 5. A small portion was immediately disintegrated in a British disintegrator for 7500 revolutions. The x-ray diffractogram is shown in Figure 6 and the crystallinity calculated therefrom is 70%. A third portion of the sample was beaten in a Jokro mill for 140 min., and the crystallinity of the sample was found to be 84%. The x-ray diffractogram is presented in Figure 7. The crystallinity index values obtained from the present investigation are calculated from the formula, $100(I_{max} - I_{min})/I_{max}$.

It is seen from the above experimental results that cellulose treated with anhydrous ethylamine and then extracted with chloroform at elevated temperature gives a higher value of crystallinity than a water-washed sample, while beating the ethylamine-treated cellulose restored the crystallinity completely.

Effect of Time on Crystallinity of Ethylamine-Treated Cellulose

Cotton linters, treated with 99.8% ethylamine, were washed with ice cold water. A part of this pulp was stored in the wet condition in a room at

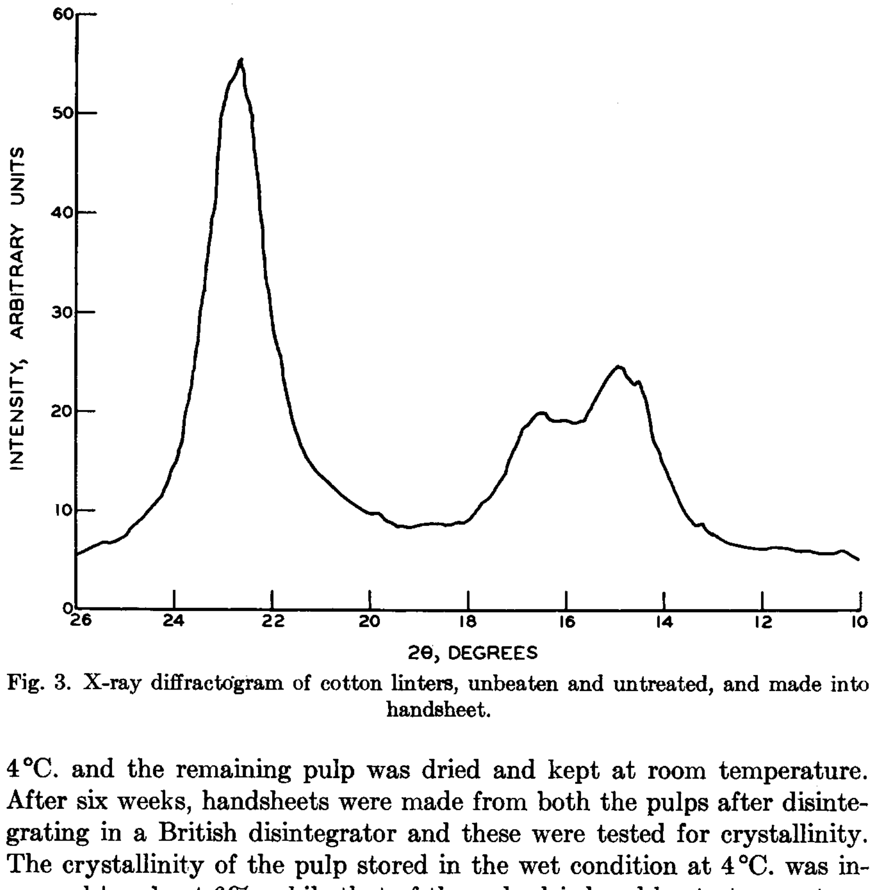

Fig. 3. X-ray diffractogram of cotton linters, unbeaten and untreated, and made into handsheet.

4°C. and the remaining pulp was dried and kept at room temperature. After six weeks, handsheets were made from both the pulps after disintegrating in a British disintegrator and these were tested for crystallinity. The crystallinity of the pulp stored in the wet condition at 4°C. was increased by about 6%, while that of the pulp dried and kept at room temperature was increased by 14%. The x-ray diffractogram of this pulp is given in Figure 8. These results indicate the slow restoration of crystallinity.

CONCLUSIONS

Cellulose can be swollen with several swelling agents. In order that these may be removed, various techniques have been employed and have been reported in the literature. For example, if water is used as a swelling agent, the solvent replacement method could be used for removal. In this case, a lower value of crystallinity is observed[4] than if water were removed by drying. On the other hand, if ethylamine is used as a swelling agent, it can be removed either by water, pyridine, or chloroform. Water has been used for removal by some investigators,[7,8] while pyridine has been used by others.[12] Chloroform has been used for extraction by Segal et al.[2,11] and by the authors. In all these cases, the amount of decrease observed in the crystallinity depends on the method of ethylamine removal. All these changes in crystallinity could be attributed to the swelling of cellulose

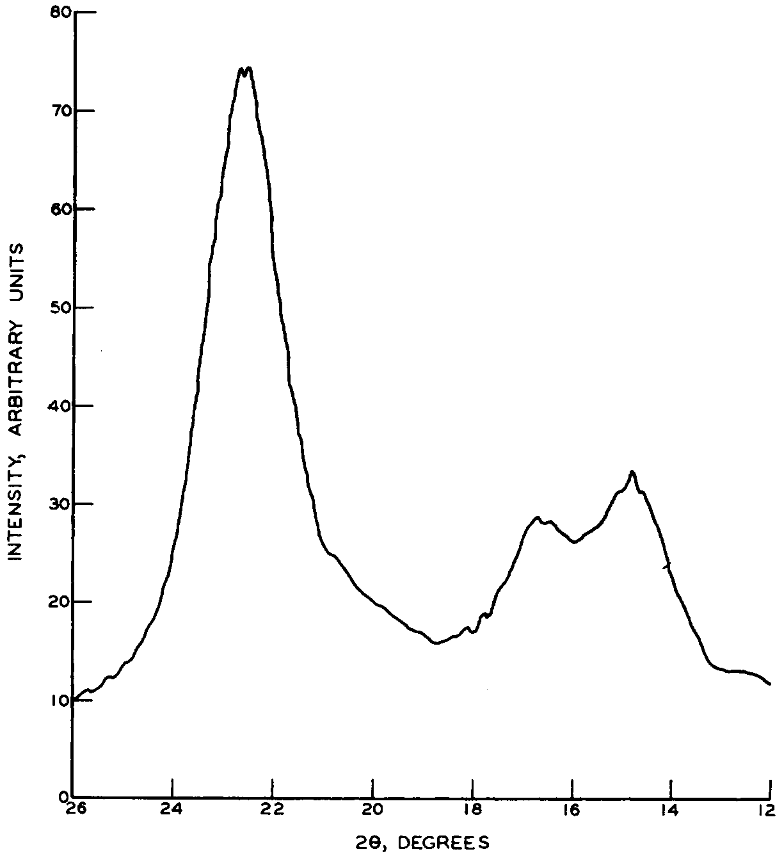

Fig. 4. X-ray diffractogram of cotton linters treated with 99.8% ethylamine, beaten for 215 min. and made into handsheet.

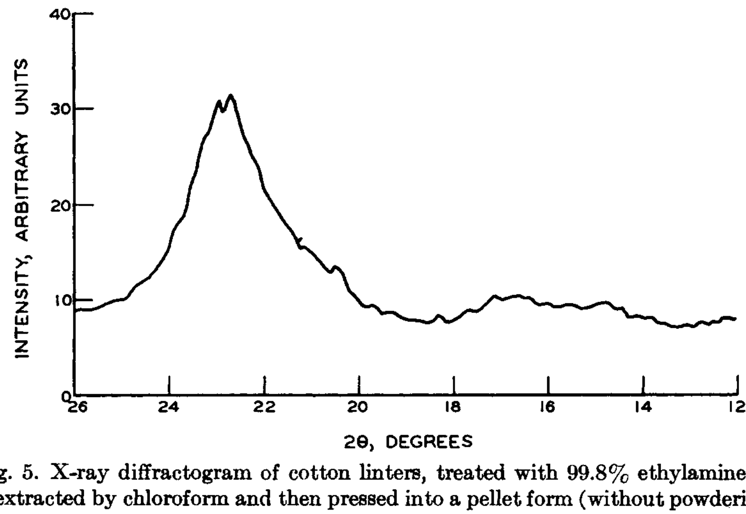

Fig. 5. X-ray diffractogram of cotton linters, treated with 99.8% ethylamine which was extracted by chloroform and then pressed into a pellet form (without powdering in a Wiley mill) at 2500 psi.

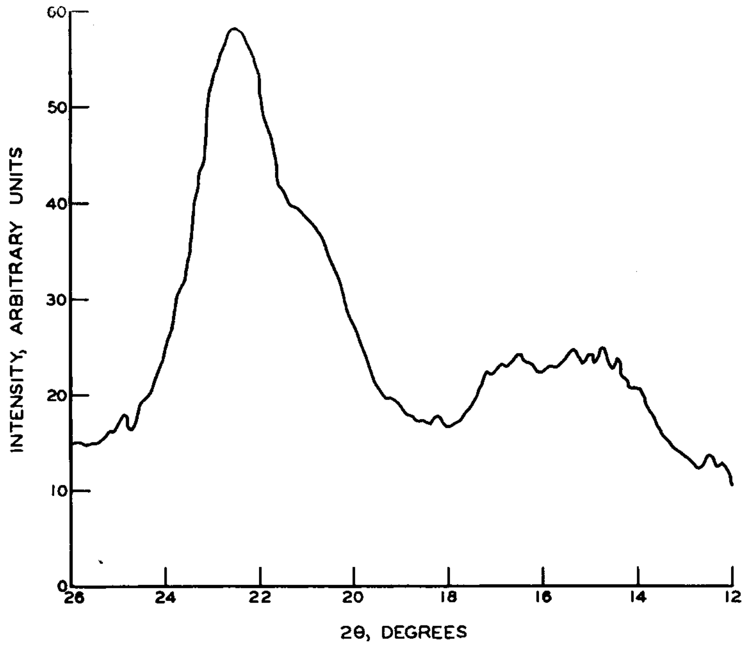

Fig. 6. X-ray diffractogram of cotton linters, treated with 99.8% ethylamine, extracted with chloroform, and made into handsheet.

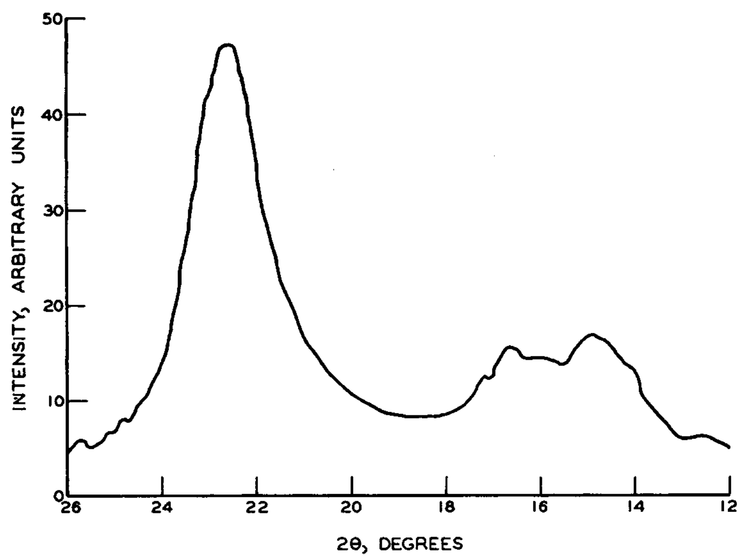

Fig. 7. X-ray diffractogram of cotton linters treated with 99.8% ethylamine, extracted with chloroform, beaten for 215 min. in a Jokro mill, and then made into handsheet.

resulting in an apparent change in crystallinity taking place mainly in the disordered regions of cellulose. If ethylamine is removed by pyridine at room temperature, a maximum change in moisture regain is observed.[12] Water, (0°C. or room temperature) if used as a removal agent, causes a smaller change in crystallinity in comparison with the result obtained with pyridine. If chloroform at 60°C. is used for removal, then most of the change in crystallinity is restored. The x-ray diffractogram for this is given in Figure 5. Segal et al.[2] have reported that cotton immersed for 4 hr. in anhydrous ethylamine and then immersed overnight in anhydrous hexylamine shows 46% crystallinity (acid hydrolysis) when the amines are

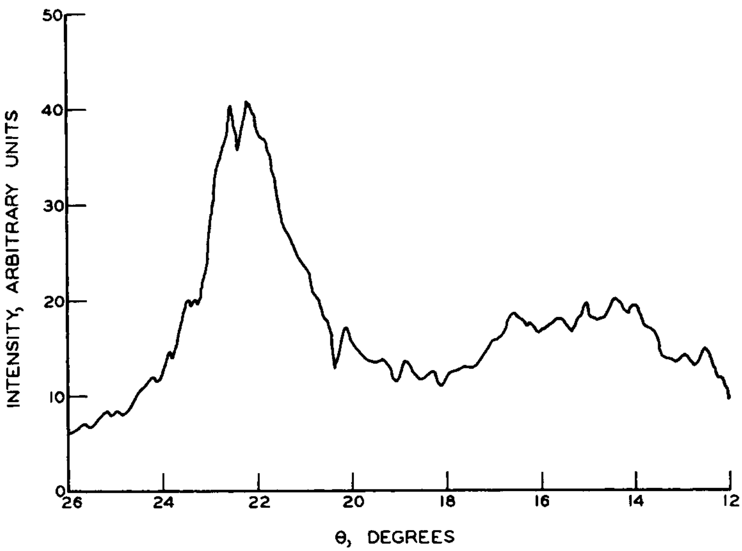

Fig. 8. X-ray diffractogram of cotton linters, first beaten for 140 min., then treated with 99.8% ethylamine, washed with water, kept for 6 weeks at room temperature, and made into handsheet.

removed at an elevated temperature in a Soxhlet apparatus. This low value of crystallinity persists even when the sample is immersed in boiling water for 4 hr. This discrepancy might be due to the incomplete removal of hexylamine. From the results of this and previous investigations,[5,6,10] none of these changes appear to be permanent.

Although some interesting results regarding the apparent decrease in crystallinity are obtained by using various washing agents to remove ethylamine from cellulose, of particular interest is the substantial effect of beating after ethylamine treatment in causing the crystallinity to increase toward the initial value. It has been reported earlier[10] that beating of ethylamine-treated cellulose not only restores the crystallinity but also restores the dielectric constant and density of cellulose.[10] If cotton linters are beaten for a period of time and their crystallinity measured by x-ray diffraction, no appreciable change in crystallinity is observed.

In conclusion, the authors would like to suggest that decrystallization in the so-called crystalline region does not occur in cellulose by ethylamine treatment and that the change observed could be due to swelling causing a further apparent change in the lateral order structure in the so-called "amorphous" portion of cellulose. These apparent changes can be restored quickly by beating, or partly restored by boiling in water, or more slowly, by keeping the treated sample at room temperature in a moist atmosphere.

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Résumé

On présente les résultats de l'influence d'un traitement à l'éthylamine dans différentes conditions sur la cristallinité de la cellulose. La façon d'éliminer de la cellulose l'agent gonflant est importante pour déterminer l'importance du changement de la structure latérale de la cellulose. Il semble que le changement de la cristallinité observée pendant le traitement avec l'éthylamine est due au gonflement de la cellulose, qui produit un désordre uniquement dans la partie amorphe de la cellulose.

Zusammenfassung

Ergebnisse der Einwirkung einer Äthylaminbehandlung auf die Kristallinität von Zellulose unter verschiedenen Bedingungen wurden vorgelegt. Die Art und Weise der Entferunung des Quellungsmittels aus der Zellulose ist für die Bestimmung des Betrages der Änderung der seitlichen Ordnungsstruktur der Zellulose von Bedeutung. Es scheint, dass die bei der Äthylaminbehandlung beobachtete Kristallinitätsänderung auf die Quellung der Zellulose zurückgeführt werden kann, wodurch eine Unordnung nur im sogenannten amorphen Bereich der Zellulose entsteht.

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