

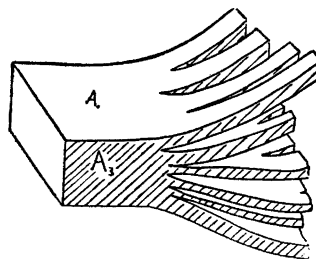
## Swelling and Heterogeneous Hydrolysis of Cotton Linters and Wood Pulp Fibers Related to Their Fine Structure

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The dual fine structure of all kinds of cellulose fibers, that is, the arrangement of the cellulose chain molecules in regions of high lateral order ("crystallites") and in regions where the lateral order is lower ("amorphous regions"), is today well established. There is a gradual transition from the symmetrical three-dimensional arrangement in the crystallites to an eventually highly disordered state in the amorphous regions. Hermans<sup>1</sup> has pictured the arrangement of the transition areas as shown in Fig. 1. Due to preferential cleavage of the crystallites along plane  $A_0$ , the leaflet structure shown will be typical for the transition of a crystallite into the disordered state.

Compared with the length of the cellulose molecule, the size of the regions exhibiting high lateral order is relatively small. In an undegraded native fiber, each cellulose chain will pass through a relatively high number of crystallites. The degree of order and the relative amount of transition regions are therefore of the greatest importance to the behavior of the fibers, especially in reactions which, at least in their initial state, involve little or no swelling of the fibers. There is no necessity to assume that the transition areas are similar for all kinds of cellulose fibers. On the contrary, it seems reasonable to assume that the conditions prevailing when the cellulose chains



*Fig. 1. Diagram of cellulose crystallite and its transition regions according to Hermans<sup>1</sup>.*

arrange themselves, *e.g.* the amount of noncellulosic materials present, may greatly influence the final arrangement and the extent of these regions.

During heterogeneous hydrolysis of cellulose fibers, the chains in the disordered areas are attacked first, and part of them are cleaved and brought into solution as glucose or small chain fragments. Based upon this principle, Nickerson<sup>2</sup> introduced a method where the loss in material is regarded as an expression for the percentage of "crystallinity" in a fiber. Similar procedures were applied later by several investigators<sup>3-6</sup>. It has, however, been suggested<sup>7, 8</sup> and recently conclusively shown<sup>9</sup> that, at least in regenerated fibers, the amount of the ordered areas increases upon hydrolysis. Besides the determination of loss of material, much interest has been focused on the constant average degree of polymerization (limit DP), which the hydrolyzed material assumes after a certain time of hydrolysis. This limit DP is thought to be similar to the original crystallite size.

Less attention has been directed to the rate of drop in DP during the hydrolysis process. One of the reasons may be that many of the investigators used fibers — refined and swelled cotton and wood pulps and regenerated fibers — where the drop in DP to a constant value takes place almost instantaneously under the applied conditions. It is, however, to be expected that with suitable conditions, the rate of decrease in the average DP will be greatly influenced by the arrangements in the disordered regions and should furnish valuable information.

Due to the "recrystallization", the limit DP will not be a direct measure of the length of the crystallites. It might, however, be expected to bear a close relationship to the length of the crystallites, and to that part of the transition areas and molecular fringes which, because of an appropriate arrangement, will rearrange into a closer packed system.

We have recently<sup>10</sup> shown that native cotton linters and wood pulp fibers behave quite differently during heterogeneous hydrolysis, both under mild and relatively severe conditions. Whereas the degradation of cotton linters proceeds rapidly and the hydrolyzed material almost instantly reaches a constant limit DP value, the degradation of wood pulp fibers is rather slow and the limit DP value is approached gradually. Fig. 2, taken from<sup>10</sup> illustrates clearly the contrast in the degradation of these two fibers during heterogeneous hydrolysis.

The present paper deals with further investigations on this difference between cotton linters and wood pulps. Pulp fibers, cooked to different average degrees of polymerization, and cotton linters are swelled in alkaline solutions of increasing swelling power. The fibers thus treated are hydrolyzed, and the rate of loss of material and the drop in DP, together with the

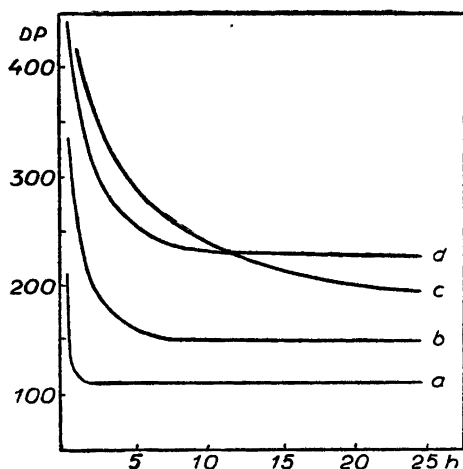


Fig. 2. Drop in DP during heterogeneous hydrolysis for a: Cotton linters, b: Rayon pulp, c: Unbleached rayon pulp, d: Extracted holocellulose, from (10).

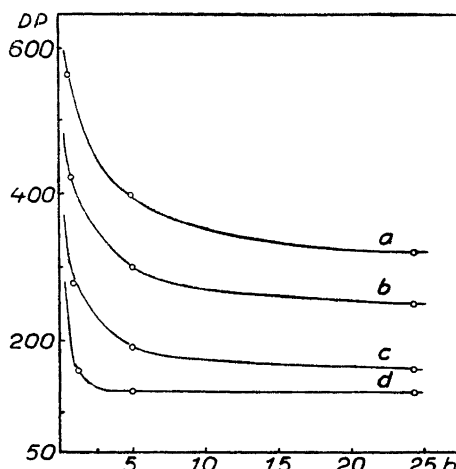


Fig. 3. Drop in DP during heterogeneous hydrolysis of a: High viscosity pulp, b: Medium viscosity pulp, c: Low viscosity pulp, d: Cotton linters (Italian),

limit DP values, are determined. The water absorption data for the swelled and hydrolyzed materials are also measured. A considerable dissimilarity is found to exist between the cotton linters and wood pulp fibers. This dissimilarity is considered in relation to the known fine structure of fibers, and can be explained by assuming a different arrangement of the transition and disordered areas in these two fibers.

EXPERIMENTAL

Materials

One sample of cotton linters was of Italian origin, carefully bleached but not further refined. The another sample was an acetate grade linters from Hercules Powder Co.\*. The pulps were chlorine bleached sulfite spruce pulps made either in the laboratory or commercially. The following analytical data according to CCA standard methods may be regarded as average values:

$\alpha$ -Cellulose	87	— 89	%
Pentosan	1.0	— 1.2	»
Lignin	0.3	— 0.6	»
Ash	0.08	— 0.10	»

\* We wish to express our gratitude to Dr. H. M. Spurlin, Hercules Powder, Co., Wilmington, Del. USA, who kindly furnished us with this material.

The average DP's varied as shown in the tables. All samples were extracted with alcohol — benzene (1 : 2) for 24 hrs, and air dried.

### Methods

*Swelling* was accomplished with sodium hydroxyde solutions of 0 (water) — 2—4—6—8 and 10 per cent by weight at 3° C for 2 hrs. Under these conditions, ten per cent alkaline solution will cause intracrystalline swelling. The swelling solution (500 ml to 15 g of fibers) covered the fibers completely. The fibers were recovered by washing carefully with ice water several times, leaving in water overnight at room temperature, washing again with a large amount of water and finally with acetone, and then air dried. The loss of material caused by the swelling was found by determining the carbohydrates in the combined filtrate and wash-water. The values thus obtained checked very well with the recovered material. The swelling caused no decrease in the viscosity average DP, in fact a small increase was observed, due to dissolution of low-molecular materials.

*Hydrolysis* was carried out with 2.5 *N* H<sub>2</sub>SO<sub>4</sub> in a thermostat regulated to 97° C ( $\pm 0.2^\circ$  C). A special hydrolysis apparatus was used which allowed fresh acid to flow continuously through the material during the hydrolysis\*. By carrying out the hydrolysis in this way no humidification or darkening of the material takes place. The amount of reducing sugar was determined at appropriate times as glucose in the hydrolyzate, *i. e.* in the acid leaving the apparatus. When used for further studies, the hydrolyzed material was washed with hot water, dilute ammonia and again with hot and cold water, finally with acetone, and dried under vacuum at 60° C for 12 hours. The yield determined in this way checked fairly well with the glucose determinations, the former usually being one to two per cent lower. The yield values in the tables refer to the glucose determinations.

The viscosity DP's were determined by converting to the nitrate and determining the intrinsic viscosity in acetone solution by the method described earlier<sup>10</sup>, and in viscometers similar to those described by Wagner<sup>11</sup>. Correction was made for kinematic error. The intrinsic viscosities were converted to DP's using Staudinger's equation with  $K_m = 10^{-3}$  (*c* in g/l). The water regain was determined at 55 % rel. humidity (over 40 weight per cent H<sub>2</sub>SO<sub>4</sub> at 25° C) on materials dried in a vacuum oven at 60° C for 24 hrs, and over P<sub>2</sub>O<sub>5</sub> at room temperature for several days.

### EXPERIMENTAL RESULTS

The drop in DP during the hydrolysis of three pulps, cooked to varying viscosities, and the cotton linters is shown in Fig. 3. All samples were swelled in water only. The same difference as found earlier<sup>10</sup>, in the behavior of cotton linters and wood pulp fibers is demonstrated here to an even greater extent. Already after 4—5 h, the DP of the linters reaches a constant limiting value. The decrease in DP of the wood pulps is again much slower, and the limit DP value is approached gradually and apparently is not reached

\* For informations regarding this apparatus we are indepted to Dr. W. E. Rosevear, E. I. du Pont de Nemours (through professor C. B. Purves, Mc Gill University, Montreal, Canada).

*Table 1. Drop in degree of polymerization for wood pulp dependent upon time of hydrolysis and previous swelling.*

Material	Swelled in NaOH Weight %	Degree of polymerization after hydrolysis in hours		
		1	5	24
High viscosity pulp (DP = 1950)	0	560	400	310
	2	510	330	270
	4	370	275	240
	6	200	170	160
	8	90	60	60
	10	70	60	60
Medium viscosity pulp (DP = 1300)	0	410	300	240
	2	380	275	230
	4	330	250	225
	6	220	180	170
	8	75	65	60
	10	60	55	55
Low viscosity pulp (DP = 850)	0	275	195	165
	2	265	190	160
	4	235	175	150
	6	140	125	115
	8	60	60	50-55
	10	55	50	45-50
Very low viscosity pulp (DP = 500)	0	255	190	160
	4	215	170	145
	6	95	85	85
	8	55	45	40-45
	10	50	45	40-45

even after 24 h. Fig. 4 (upper curve) indicates that, under the applied conditions, 30-40 h. are necessary before the hydrolysis curve levels off at an apparently constant value.

The limit DP of the pulps is apparently not constant but depends greatly upon the degree of cooking, decreasing as the viscosity of the pulp decreases. The limit DP of the high viscosity pulp is about 300 while that of the low viscosity pulp is only 160. All of the limit DP's of the unswelled pulps are therefore higher than the limit DP found for the cotton linters (130-140), but approach this value as the severity of the cooking increases. It should be noted that the slopes of the hydrolysis curves for the pulps remain nearly constant after about two hours, regardless of the degree of cooking.

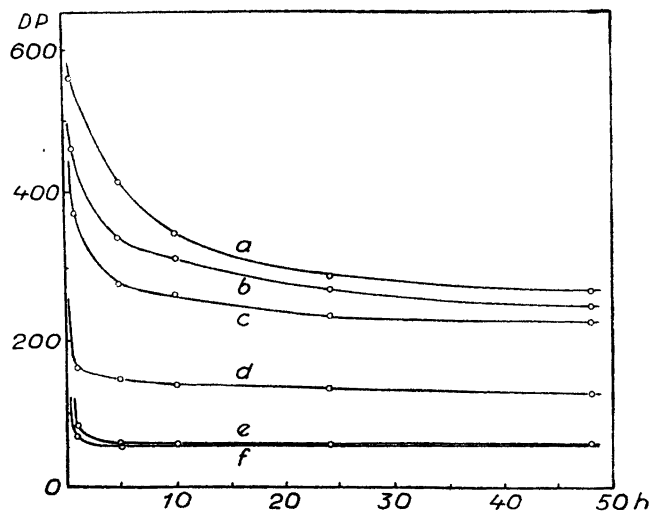


Fig. 4. Drop in DP during heterogeneous hydrolysis of a pulp swelled in a: Water, b: 2 % NaOH, c: 4 % NaOH, d: 6 % NaOH, e: 8 % NaOH, f: 10 % NaOH.

Table 1 shows the pronounced influence alkaline treatment exerts on the hydrolysis of the pulps. For one particular pulp, not included in Table 1 but later used for determinations of dissolved material during hydrolysis, similar data for a longer time of hydrolysis are plotted in Fig. 4. Even swelling in two and four per cent solutions increases the rate of degradation and results in a somewhat lower limit DP. Swelling in six per cent solution has a marked influence, not only upon the hydrolysis rate but also upon the limit DP value. When the strength of the swelling solution is raised to eight per cent, a sharp increase in the rate of hydrolysis occurs, and the limit DP value, which now is very low, is reached almost instantly. When swelled in a ten per cent alkaline solution, further change in the behavior of the pulp is very small. The limit DP value for all the pulps is almost the same after being swelled in eight or ten per cent alkaline solution, regardless of the original DP; whereas the limit DP's for samples swelled in the intermediate concentrations vary widely with the degree of cooking. As can be seen from Table 2, the alkaline swelling of the cotton linters do not show the same effect as described for the wood pulps. The rate of drop in DP changes very little and the limit DP hardly at all as the strength of the alkaline swelling solution is increased from zero to eight per cent. When the strength reaches ten per cent, the rate of decrease in DP is somewhat faster and the limit DP is lowered.

In Fig. 5 and Fig. 6, dissolved material is plotted against time of hydrolysis for one of the pulps and the acetate grade cotton linters, swelled in alkaline

Table 2. Drop in degree of polymerization for cotton linters dependent upon time of hydrolysis and previous swelling.

Material	Swelled in NaOH Weight %	Degree of polymerisation after hydrolysis in hours		
		1	5	24
Italian origin	0	160	140	140
	2	155	140	140
	4	155	140	140
	6	145	140	140
	8	145	140	140
	10	105	90	85
Acetate grade from Hercules Powder	0	155	140	140
	4	155	140	140
	6	155	140	140
	8	145	130	130
	10	85	80	80

solutions of increasing strength. For the pulp, the amount of material dissolved is seen to decrease at first as the strength of the alkaline solution is increased from zero to four per cent. For a material swelled in six per cent solution, the amount dissolved is somewhat higher than for the untreated material; and still higher for material treated with eight and ten per cent alkali. The increase is, however, rather small.

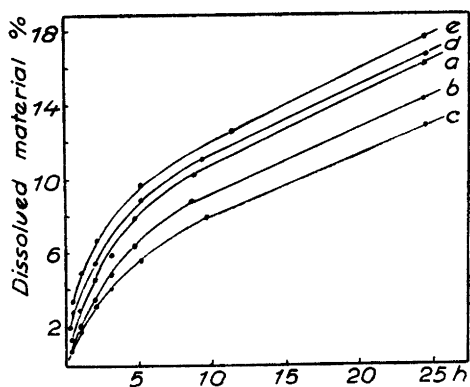


Fig. 5. Loss in material during heterogeneous hydrolysis of a pulp swelled in a: Water, b: 2 % NaOH, c: 4 % NaOH, d: 6 % NaOH, e: 8 and 10 % NaOH.

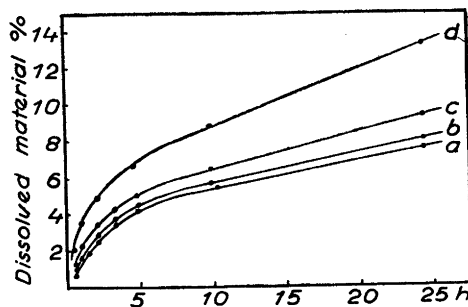


Fig. 6. Loss in material for cotton linters swelled in a: Water, b: 2, 4 and 6 % NaOH, c: 8 % NaOH, d: 10 % NaOH.

The decrease in the loss of material shown in the two and four per cent curves is caused by the dissolution of easily hydrolyzable material during the alkaline swelling. These losses amount to 2.5 and 5.8 per cent, respectively. The dissolution during the swelling explains also the small increase in hydrolyzed material represented by the six, eight and ten per cent curves. In these cases, the swelling losses were higher, amounting to 12 per cent for the first and 16—17 per cent for the last two samples. It is, however, remarkable that these samples, which behaved so differently when the effect of the hydrolysis was measured with regard to drop in DP's, are so similar in their yield curves. Table 3 demonstrates clearly that the amount of material dissolved during hydrolysis changes only slightly with increasing swelling, in spite of large decreases in DP.

*Table 3. Degree of polymerization and loss in material after five hours of hydrolysis dependent upon degree of swelling.*

Material	Swelled in NaOH Weight %	DP	Loss in material %
Cotton linters (Italian)	0	140	4.3
	2	140	4.1
	4	140	4.1
	6	140	4.1
	8	130	4.4
	10	90	6.2
High viscosity pulp	0	400	9.4
	2	330	7.5
	4	275	6.2
	6	170	6.6
	8	60	9.2
	10	60	9.6
Medium viscosity pulp	0	300	6.7
	2	275	5.5
	4	250	5.3
	6	180	5.6
	8	65	8.5
	10	55	8.9
Low viscosity pulp	0	195	6.4
	2	190	5.6
	4	175	5.1
	6	125	6.6
	8	60	8.9
	10	50	8.8

It should be noted that the slopes of the linear parts of the yield curves (Fig. 5) are almost alike for all pulp samples, and only a very small increase is observed for the eight and ten per cent curves. This shows that, after dissolution of the easily hydrolyzable part, the attack on the ordered parts is not appreciably influenced by the previous swelling.

For the cotton fibers (Fig. 6), very little change in the yield curves occurs up to swelling in six per cent solution. A small increase is observed for the eight per cent curve. The first notable increase in loss of material takes place, however, when the linters are swelled in the ten per cent solution. The slopes for the linear parts of the yield curves are seen to be alike up to eight per cent followed by a much steeper curve for the material swelled in a ten per cent solution. This shows that the attack on the more ordered parts of cotton linters is greatly increased when the alkaline solution is strong enough to cause intracrystalline swelling.

Table 4 shows the relative water regains for one of the linters and pulps for samples swelled but not hydrolyzed. The relative regains are obtained by choosing the regain of the water swelled sample as unity. The measured regains are given in column three. Due to dissolution of material during the swelling, these values do not give a correct picture of the increase in disordered areas caused by the swelling. Assuming that the amount which went into solution belonged to the highly disordered part and would have formed Cellulosehydrate II ( $C_6H_{10}O_5 \times 1\frac{1}{2} H_2O$ ) under the conditions employed, the values in column five are obtained. Based on these data, it is seen that for the cotton, swelling in up to six per cent alkali causes little change, swelling in an eight per cent solution increases the water regain somewhat, but the only large increase, from 1.12 to 1.56, is found when the linters are swelled in ten per cent lye. The pulp samples show a continuous increase from 1.0 to 1.10 when swelled in solutions from zero to four per cent. A sharper increase, bringing the regain to 1.27, is found for the sample swelled in six per cent lye, and a larger jump in the regains, from 1.27 to 1.70, is observed when an eight per cent solution is employed. No further increase occurs when the strength of the swelling solution is raised to ten per cent.

The water regains in column three should be an expression for the relative amounts of disordered material present in the swollen samples. It is surprising that the marked differences between the pulp samples in the rate of hydrolysis, expressed as drop in DP, are not reflected in their regains. No change in the regains occurs for samples swelled in lyes of zero, two, and four per cent, and only a relatively small increase is found for the six per cent sample, whereas the hydrolysis rate showed a marked difference for these samples (Fig. 4 and Table 1). A more pronounced increase in the water regains

Table 4. *Relative water regains for cotton linters and wood pulp dependent upon degree of swelling.*

Material	Swelled in NaOH Weight %	Measured water Regain *	Material dissolved %	Corrected water regain *
Cotton linters (Italian)	0	1.00	—	1.00
	2	1.00	0.6	1.01
	4	1.05	0.6	1.06
	6	1.05	0.6	1.06
	8	1.08	1.2	1.12
	10	1.44	2.2	1.55
Low viscosity pulp	0	1.00	—	1.00
	2	1.00	2.0	1.04
	4	1.00	3.7	1.10
	6	1.07	6.5	1.27
	8	1.36	12.0	1.70
	10	1.36	13.5	1.74

is noticed for the eight and ten per cent samples and is in accordance with the hydrolysis rate.

It is interesting to note that the water regain for the cotton linters has the most pronounced increase between the eight per cent sample (1.08) and the ten per cent sample (1.44), in accordance with earlier data<sup>12</sup>. For the pulp samples, this pronounced increase (from 1.07 to 1.36) takes place already for samples swelled in eight per cent NaOH, and no further increase is observed when ten per cent solution is employed.

Table 5 shows the absolute water regains for cotton linters and two pulp samples prior to hydrolysis, and the minimum water regains obtained during the hydrolysis. The minimum values were reached after one hour of hydrolysis. It is seen that the regains of the wood pulp, before as well as after hydrolysis, are always higher than those of the linters. The regains for the hydrolyzed pulp samples are seen to decrease with swelling solutions of concentrations up to six per cent, after which a sharp increase occurs. The regain for the hydrolyzed cotton remains constant up to the ten per cent sample, which shows a much higher regain.

\* Water regain for material swelled in water chosen as unity.

Table 5. Absolute water regains for cotton linters and pulps before and after hydrolysis, dependent upon degree of swelling.

Materials	Swelled in NaOH Weight %	Water regain prior to hydrolysis %	Minimum water regain after hydrolysis
Cotton linters (Italian)	0	4.9	4.3
	2	4.9	4.2
	4	5.1	4.3
	6	5.1	4.3
	8	5.3	4.2
	10	7.2	5.0
Medium viscosity pulp	0	6.4	5.7
	2	6.4	5.7
	4	6.4	5.6
	6	6.7	5.3
	8	7.8	5.8
	10	7.7	5.8
Low viscosity pulp	0	5.9	5.4
	2	5.8	5.3
	4	5.8	5.2
	6	6.2	5.1
	8	7.8	5.9
	10	7.7	6.0

## DISCUSSION

The explanation for the differences exhibited by the cotton linters and wood pulp fibers during heterogeneous hydrolysis must be sought in divergences in their fine structures. The recent works of Rånby<sup>13</sup> and Rånby and Ribi<sup>14</sup> have made it plausible to assume that the size of the regions exhibiting high lateral order do not vary much between native cotton and wood pulp fibers, being in the order of 120—140 glucose anhydride units. The difficulty in obtaining this low limit DP for the pulp fibers in contrast to the linters (Table 1), shows that the supermolecular arrangement between the crystallites cannot be the same in these two fibers.

The intercrystalline arrangement in the linters obviously allows the acid to penetrate without difficulty and cleave the cellulose chains into fragments, the size of which is not affected by prolonged hydrolysis nor by intercrystalline swelling solutions. The penetration of the acid into the intercrystalline por-

tions of the pulp fibers is, however, clearly hindered, and the cellulose chains are cleaved at fewer places than are the chains in linters. The size of the fragments formed is apparently not constant but depends upon the severity of the cooking conditions and even more upon the degree of swelling the pulp may have undergone.

In Fig. 7 a and b, proposed arrangements for the fine structures of linters and wood pulp fibers are schematically pictured. These are in agreement with the outline above and will be seen to explain the experimental observations.

The leaflet transition regions in the linters are supposed to be relatively short and rapidly develop into molecular fringes (Fig. 7 a). The chains in the loose molecular fringes will be easily available for acid attack and this explains the rapid drop in DP during hydrolysis. The fragments formed will, perhaps after some rearrangements, mainly consist of single crystallites. Intercrystalline swelling will have little influence upon the limit DP because the transition regions soon reach a high degree of order, which is not effected by swelling agents of this type. It will be recalled (Table 1) that swelling in alkaline solutions from zero to eight per cent did not influence either the rate of hydrolysis or the limit DP. It was only when the solution caused intracrystalline swelling (10% NaOH) and was transformed to Cellulose II that the limit DP showed some decrease.

For the wood pulp fibres it is proposed that the leaflet, perhaps mainly of a two-dimensional, arrangement regarded as typical for the transition areas, partially extends throughout the intercrystalline regions (Fig. 7 b). The crystallites would thus be interconnected by molecular arrangements exhibiting a certain degree of order, as well as by single cellulose chains. Such an intercrystalline arrangement would be partly resistant towards acidic agents under not too severe conditions. The hydrolysis product would therefore consist not only of single crystallites but perhaps mainly of two or several crystalline regions joined through one or more acid resistant leaflet structures. In agreement with this it was found that the limit DP of native fibers which had not been exposed to too severe cooking conditions (the two first samples in Table 1) was much larger than that corresponding to the crystallite size according to Rånby and Ribi.

The intercrystalline arrangements discussed above would be susceptible to swelling solutions and might be expected to be destroyed by solutions of relatively low swelling power. It was also found (Table 1 and Fig. 4) that the rate of hydrolysis increased and the limit DP decreased as the swelling power of the alkaline solution was raised. The gradual decrease in limit DP with increasing swelling power indicates that the proposed intercrystalline

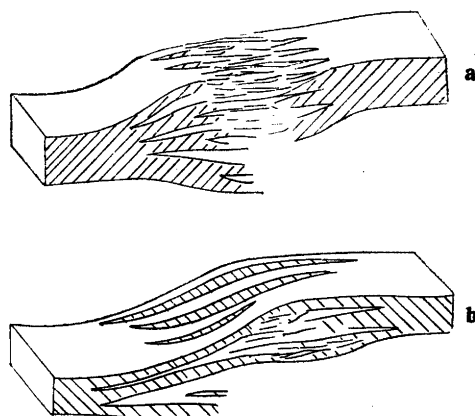


Fig. 7. Proposed arrangements for the intercrystalline structure in a: Cotton linters, b: Wood pulp fibers.

arrangements are destroyed successively and thus exhibit a wide range of orderliness.

It might be mentioned at this stage, that the material used by Rånby and Ribí<sup>14</sup>, as representative of a pulp fiber and designated "wood pulp", was a refined sulfite spruce pulp sample\*, whose hydrolysis behavior was found in this laboratory to lie somewhere between the values given by four and six per cent samples of the "Low viscosity pulp" in Table 1. On hydrolysis such a material might be expected to yield a relatively large amount of individual crystallites, or more correctly secondary crystalline fragments, which are found to have a limit DP very close to that of cotton linters, namely 110—140 for the former, against 130—140 for the latter. The limit DP value for the six per cent sample of the "Very low viscosity pulp" (Table 1) is, however, seen to be lower (80—85) than the DP of the crystallite proposed by Rånby and Ribí, and suggests that the size of the regions of high lateral order in wood pulps is smaller than those in cotton linters.

It must be regarded as significant that the lowest limit DP values, as well as the highest water regains (Table 4), in case of the pulps, were reached for samples swelled in an eight per cent NaOH solution, whereas a ten per cent solution was necessary for the linters. This indicates that for the pulps the transition from Cellulose I to Cellulose II occurs at conditions which are considered to cause intercrystalline swelling only<sup>15</sup>. This suggests that there might exist a difference also in the orderliness or in the form of the regions exhibiting high lateral order in wood pulp and cotton fibers. It will be recalled that the linear part of the yield curves were steeper for the pulp than

\* Private Communication from Mr Rånby.

for the linters (Figs. 5 and 6), indicating that the crystalline regions are more susceptible for attack in pulps than in linters. Table 5 showed that the water regains after hydrolysis were higher for the pulps than for the linters, showing that in the former, in spite of similarity in crystallinity of these two fibers<sup>16</sup>, more hydroxyls are available for absorption of water; that is, the ordered regions in pulp fibers seem to have a larger surface than the crystallites in cotton linters. It might therefore be supposed that the crystalline regions in wood pulp fibers are flatter, more ribbonlike, than those regions in cotton linters.

The proposed fine structural differences between wood pulp and cotton linters are naturally outlined only very schematically. Further investigations of both a chemical and physical nature are necessary before a more detailed picture can be presented. It might not be unreasonable to assume that other pure cellulose fibers, *e.g.* cotton and ramie, have fine structures similar to cotton linters, whereas all wood pulp fibers have fine structures more similar to that proposed for the spruce pulp fibers.

#### SUMMARY

Comparative hydrolysis has been carried out on cotton linters and wood pulp fibers. Whereas linters are rapidly degraded to a constant limit DP, the degradation of wood pulps is much slower and a limit DP is reached only after prolonged hydrolysis. The limit DP depends greatly upon the severity of cooking.

Swelling in alkaline solutions from zero to eight per cent has no effect on the degradation of linters. A somewhat lower DP is obtained for samples swelled in ten per cent solution. The effect of a similar swelling on pulps is remarkable. Even swelling in alkaline solutions of low concentrations exerts a pronounced influence upon the degradation. A fast degradation to a low limit DP is obtained for samples swelled in eight per cent alkaline solution. No further change is observed when the concentration is raised to ten per cent.

For cotton a significant increase in dissolved material during hydrolysis and in water regains occurs when samples are swelled in ten per cent alkali. Only a small increase was found in the yield curves for the pulps and the large increase in the water regains took place already for samples swelled in eight per cent alkali.

It is supposed that these dissimilarities between cotton linters and wood pulp fibers are due to differences in their fine structures. Arrangements are proposed, assuming looser molecular packing in the disordered regions and rather short transition areas for the linters, and a somewhat higher order in

the disordered regions and relatively extended transitions regions for the pulp fibers. In the pulp fibers the crystallites are proposed to be somewhat shorter and flatter than in linters.

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