THE EFFECT OF WATER REMOVAL ON THE CRYSTALLINITY OF CELLULOSE

A Thesis

by

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A B S T R A C T

The effect of various modes of drying upon the crystallinity of cellulose has been determined by X-ray diffraction.

No change in the crystallinity index was observed when previously undried pure cellulose fibers from softwood were dried from water under a wide range of conditions, but a lower value was obtained when dried from benzene to which the fibers were accommodated by a series of solvent exchanges. Heat of wetting determinations on the same samples indicated changes in the accessibility with different drying methods. Qualitative variations in the degree of intra-fiber bonding were also detected by a differential staining method. The X-ray measurements suggested that drying from water either produces no change in lateral order or that such changes are too small to be detectable by X-rays.

The crystallinity of cellulose prepared by dry-milling whole fibers was studied. The crystallinity was substantially reduced in a Wiley mill and obliterated in a ball mill. X-ray diffraction showed that wetting with water and then drying restored the crystallinity, while similar treatment with other liquids yielded less

definite results. However, by following the destruction of the (021) lattice with progressive periods of milling, it was tentatively inferred that alcohols reform this lattice to a limited extent depending, among other factors, upon the swelling capacity.

F O R E W O R D

This thesis has been written in a manner which, it is believed, will allow publication of its contents in a scientific journal with a minimum of revision. For the benefit of readers who do not have a specialized knowledge of the subjects discussed, particularly X-ray diffraction, and for the guidance of future workers, a number of technical terms used in the body of the thesis are defined, and additional details of experimental methods and procedures are discussed in a series of Appendices.

INTRODUCTION

The formation of intermolecular bonds between adjacent cellulose* chains by the removal of water is of considerable importance, particularly in connection with technical applications of cellulose, e.g. in textiles and in paper, and has been the subject of numerous investigations. It is now reasonably well established that most of the bonds, which can be either intra- or inter-fiber, depending upon whether or not the cellulose chains are in the same fiber, are due to hydrogen bridges*(1) between hydroxyl groups of adjoining chains.

Like the high lateral order* maintained by hydrogen-bonding in the crystalline* regions of the fibers, additional hydrogen-bonds may be expected to increase the prevailing lateral order. As a consequence, the number of available hydroxyl groups, and therefore the accessibility* of the fibers, would be reduced.

The decrease in accessibility with evaporation-drying has been amply verified by Jayme (2, 3) and Purves (4), the former by noting the decreased swelling capacity of dried fibers and the latter by applying the thallous-ethylation method.

Since the drying of cellulose is an irreversible process, any lateral order established by hydrogen-bonding may be expected to increase with repeated wetting and

*Terms marked with an asterisk are defined in Appendix I.

drying of the fibers, and cause a sharpening of the X-ray diffraction pattern of the crystalline portion. In this connection, it has been shown that the capacity of the fibers to reabsorb and retain the water decreases with the severity of drying conditions (3). Recently, it has been observed that freezing the wet fibers before air-drying the thawed material adversely affected the inter-fiber bonding of paper (5, 6). This effect was attributed to partial dehydration of the fibers as a result of freezing.

The mobility, and hence the alignment of the molecular chains in the amorphous regions of wet cellulose fibers, may be expected to be greatly reduced by freezing the water and removing it by sublimation (freeze-drying)*, or by replacing the water by a non-polar liquid (solvent-exchanged)* before drying. Fibers dried by this means would be expected to have a higher accessibility than fibers dried by evaporation of liquid water. Although little work has been done on the accessibility of freeze-dried fibers, solvent-exchanged fibers show an increase in reactivity towards various reagents. Thus Siggia (7) et al. found an increased accessibility of cotton linters to HIO_4 solution, while Conrad and Scroggie (8) found the same effect towards HCl-FeCl_3 attack. A similar trend was observed by Brown and Purves (9) in their nitration experiments on cotton linters. In addition, several

workers have shown that a reduction in inter-fiber bonding, during freeze-drying from water or evaporation-drying from a non-swelling liquid, may be responsible for adversely affecting paper strength. Van den Akker (5), Broughton and Wang (10) and Marchessault, Lodge and Mason (6) adequately demonstrated that the strength of paper handsheets dried by such methods was considerably less than the strength of normally air-dried sheets. From this it can be seen that the method of drying influences the physical properties of cellulose fibers. In turn these properties may be assumed to be closely related to the degree of hydrogen-bonding, and in turn to the lateral order introduced in the fibers by the drying operation.

The effect of different drying conditions on the crystallinity of cellulose fibers was determined by an X-ray diffraction method using the crystallinity index* parameter introduced by Ant-Wuorinen (11). This parameter may be considered to be a relative (but not absolute) measure of the fraction of crystalline material. Furthermore, it may be readily determined from the diffraction pattern. Heat of wetting determinations and a differential staining procedure were also applied to the fibers.

As the crystallinity index of whole fibers proved to be insensitive to drying, attempts were made to magnify the effects by first reducing the crystallinity by

mechanical attrition and then wetting with various liquids and drying.

The almost complete destruction of crystallinity of dried cellulose I* fibers by ball-milling has been shown by Hess (12) and by Hermans (13), using X-ray diffraction. These workers also showed that wetting the pulverized material resulted in partial recrystallization accompanied by a lattice modification to cellulose II*. In the present investigation similar behaviour was observed upon rewetting cellulose fibers, which were drastically reduced in crystallinity by dry-grinding in both a Wiley and a ball mill. However, no lattice modifications were observed on wetting. In the case of the Wiley-milled product, recrystallization was observed to occur upon exposure to water vapour of high relative humidity.

The recrystallization of mechanically degraded fibers by non-aqueous liquids has received little attention. Investigating the sorption of vapours by cellulose fibers, Kanamaru and Chao (14), Lauer (15), Stamm and Tarkow (16) found that the sorptive capacity of cotton for the normal alcohols decreased regularly with increasing molecular weight of the homologous series. From the sparse data available, it is now generally accepted that the penetration and appreciable swelling of cellulosic material can occur only with polar liquids. Furthermore, to encourage

rearrangement of the fibers and increase lateral order the swelling medium must be capable of promoting hydrogen-bonding. In this connection, it has been shown that the strength of paper handsheets made by drying from benzene was considerably less than that of handsheets dried from ethanol (10).

The variations in the crystallinity index of the mechanically degraded cellulose treated with various organic liquids appear to be consistent with the swelling capacity of the medium.

EXPERIMENTAL PART

I. MATERIALS

Cellulose Fibers

Softwood dissolving-grade sulphite pulp which had never been previously dried was kindly supplied by Fraser Companies Ltd., Campbellton, N.B., together with the following analytical data:-

Viscosity	25.4 cps.
Resin	0.37%
Pentosan	2.42%
Rayon Yield	93.7 %
10% Caustic Insoluble ...	89.3 %

Dried samples were prepared as follows:-

Sample F-1. Oven Drying at 105°C.

Sample F-2. Drying at Room Temperature (R.T.).

The drying was conducted in two stages. The pulp was first placed in a vacuum desiccator containing concentrated sulphuric acid. After about two days, when the moisture content was reduced to approximately 15%, the pulp was transferred to a desiccator containing phosphorous pentoxide and again evacuated for several days.

Sample F-3. Cyclic Wetting and Oven Drying.

After oven drying at 105°C, the pulp was suspended in water at room temperature for 24 hours, the excess water removed under mild suction and the pulp was again dried at 105°C. This operation was repeated until the sample had been exposed to ten complete drying cycles.

Sample F-4. Cyclic Wetting and Room Temperature Drying.

This sample was subjected to ten wetting and drying cycles the same as for F-3, except that each drying stage was carried out at room temperature as for F-2.

Sample F-5. Freeze-Drying from Water.

The water-wet pulp was initially frozen at -78°C by immersion in acetone/dry ice. The ice was then removed by sublimation under vacuum in a "VirTis" laboratory-model freeze-drier.

Sample F-6. Freeze-Drying from Benzene.

The water-wet pulp was suspended in 200 ccs. of acetone which had previously been distilled over activated alumina to remove traces of water. The acetone was replaced several times by a fresh batch until titration of an aliquot with Karl Fischer reagent indicated the absence of water. The pulp was then suspended in 300 ccs. of dry benzene, and allowed to stand for 24 hours in a stoppered

flask. After a further immersion of 24 hours in a fresh batch of benzene, the latter was decanted and the pulp frozen at -78°C . The benzene (m.p. 5.3°C) was removed by sublimation under vacuum as for F-5. It was noted on rewetting the sample with water that a strong odour of benzene was detectable; it has been shown that up to 1.5% benzene can be retained in this way (17).

Sample F-7. Freezing in Liquid Nitrogen.

The adverse effect of ice formation on the bonding properties of fibers has been attributed to a partial dehydration of the fibers at low temperature (6). To determine the effect of this partial dehydration on the crystallinity of cellulose, water-wet pulp was suspended in liquid nitrogen (-195.8°C) until it had frozen solidly. It was then allowed to thaw at room temperature and finally dried as for F-2.

The physical state of the dried pulp depended upon the method of drying. Evaporation of liquid water allowed the capillary forces of water to exert their influence in promoting inter-fiber bonding, and the fibers tended to be densely packed. Cyclic wetting and drying produced a bulkier pulp in which the fibers were more easily separated. Pulp which had been dried either by freeze-drying, or from a non-swelling liquid such as benzene, was even less highly bonded than when cyclically dried by evaporation of water.

Wiley-Milled Cellulose

A portion of the same batch of virgin pulp used in the preceding preparation was dried at 105°C and subsequently milled for 90 minutes in a laboratory attrition mill. A Wiley intermediate model was used for this purpose. The clearance between the stationary and revolving blades was 3×10^{-3} in. The resulting material was sufficiently fine to pass through a 60-mesh screen. Small quantities of this product were subjected to further treatment, as described below. The samples were immersed in pure liquids, having various swelling capacities, for 24 hours at room temperature and then dried as listed in Table I.

Ball-Milled Cellulose

A series of ball-milled samples of dissolving grade "Rayaceta" wood pulp were kindly supplied by Dr. J.A. Howsmon of the American Viscose Corporation, Marcus Hook, Pa. The dry material had been milled for various times up to 153 hours under the following conditions:-

Initial treatment of pulp	 Wiley Mill, 20 mesh screen.
Ball-mill charge	 1,200 gm. steel balls, 40 gm. pulp.
Mill speed	 47 r.p.m.

To follow the destructive action of ball-milling

on the crystallinity of cellulose the samples milled for progressive periods were subjected to X-ray measurements. These samples will be denoted by the letter H, followed by the number of hours milled.

In addition, small quantities of the 153-hour sample, which was completely pulverized, were subjected to various wetting and drying treatments as outlined in Table II. Except for sample B-4, the wetting and drying procedures were as for the Wiley-milled material.

The differently treated samples prepared by both types of milling remained powdery and to the eye were unchanged from the untreated material.

TREATMENT OF WILEY-MILLED SAMPLESSample

- M-1 Original milled sample.
- M-2 M-1 immersed in water, 24 hours R.T., dried at 105°C.
- M-3 Treatment for M-2 repeated 10 times.
- M-4 M-1 immersed in ethanol, 24 hours R.T., dried at 105°C.
- M-5 Treatment for M-4 repeated 10 times.
- M-6 M-1 immersed in acetone, 24 hours R.T., dried at 105°C.
- M-7 Treatment for M-6 repeated 10 times.
- M-8 M-1 exposed in a vacuum desiccator to water vapour at 93.3% R.H. for 48 hours, dried at 105°C.
-

TABLE IITREATMENT OF BALL-MILLED SAMPLESSample

- B-1 Original ball-milled sample (milled for 153 hrs.).
- B-2 B-1 immersed in water, 24 hours R.T., dried at 105°C.
- B-3 Treatment for B-2 repeated 10 times.
- B-4 B-1 treated as described for cellulose fibers (Sample F-6) with benzene removed at 105°C.
- B-5 B-1 immersed in benzene, 24 hours R.T., dried at 105°C.
- B-6 B-1 immersed in ethanol, 24 hours R.T., dried at 105°C.
- B-7 Treatment for B-6 repeated 10 times.
- B-8 B-1 immersed in acetone, 24 hours R.T., dried at 105°C.
- B-9 Treatment for B-8 repeated 10 times.
- B-10 B-1 immersed in methanol, 24 hours R.T., dried at 105°C.
- B-11 B-1 immersed in propanol, 24 hours R.T., dried at 105°C.
- B-12 B-1 immersed in butanol, 24 hours R.T., dried at 105°C.

2. EXPERIMENTAL METHODS AND RESULTS

X-Ray Measurements

General

A technique based on that of Hermans (18) was adopted for the X-ray measurements, except that air scattering was used as a reference for the incident X-ray intensity instead of a Goppel (19) camera, and the samples were mounted in the form of compressed pellets which were supported in a holder during an exposure. In addition, a nickel foil was used for absorption measurements.

Fig. 1 shows the disposition of the various parts of the camera and collimating system. The nickel-filtered copper radiation was delivered by a Muller MC-50 tube. A 9 x 12 cm. flat film camera^{*}, manufactured commercially by R. Seifert & Co., Hamburg, Germany, was used. Its collimator was replaced by a four pin-hole system and a removable nickel foil was incorporated as shown in Fig. 1.

Mounted pellets^{*} were prepared from whole fibers by separating them with two dissecting needles until the resulting material was a mass of loosely tangled individual fibers. A weight of 3 mg. $\pm$ 3% of the loose fibers was placed in a metal sample holder^{*} and compressed into a pellet by a specially-constructed press^{*}, care being taken to ensure isotropic packing in the plane of the holder. Pellets of

* Additional details of terms marked with an asterisk are given in Appendix II.

FIGURE 1CAMERA AND COLLIMATING SYSTEM

- ff' = Focal spot of Tube.
 YY' = Path of primary beam.
 aa' = Nickel filter.
 S_1S_4 = Pin-hole apertures, 1 mm.
 S_2S_3 = Pin-hole apertures, 0.7 mm.
 C = Sample.
 NN' = Nickel foil, 0.021 mm. thick,
 supported on metal frame.
 FF' = Film.
 $I_{(200)}$ = Nickel interference.
 $I_{002},$
 $I_{(101, 10\bar{1})}$ = Cellulose A_4 and A_1 interferences
 respectively.

0 2 4
cm.

the milled cellulose were formed in the same manner but with no previous scraping. For an exposure to the X-ray beam, the loaded pellet holder was mounted on the collimator. The dimensions and densities of the pellets are given in Table III.

All exposures were made at room temperature and at the prevailing relative humidity, which was in the region of 50%. Ilford - B film was used throughout*. Details of the irradiation of the samples are outlined in Table IV.

Measurements of Intensity

To determine the intensities of X-ray diffraction lines on a film, a continuous recording micro-densitometer*, manufactured by A. Kruss, Hamburg, Germany, was used. The sensitivity of the galvanometer was adjusted to give zero deflection in the unexposed region, and a full-scale deflection of 80 mm. when no light was transmitted through the film. Fig. 2 is a reproduction of a photometer trace of a diffraction pattern of wood pulp. The traces of the extreme positions of the galvanometer deflections are shown as the "zero" and "absolute black" lines. The height in mm., above the "zero" line, of any point on the trace is a measure of its intensity*. The Herzog (20) designations and Miller (21) indices* (hkl) of the principal planes of cellulose corresponding to the various peaks are included in

FIGURE 2RADIAL PHOTOMETER TRACE OF AN X-RAY DIFFRACTION
PATTERN OF WOOD PULP

- I_{as} = Maximum intensity of air scattering.
- I_{101} = Intensity of (101) peak.
- $I_{Min.}$ = Intensity of minimum point M.
- I_{021} = Intensity of (021) peak.
- I_{002} = Intensity of (002) peak.
- α = Width MW of peak (002) in radians.
- A_1, A_4 = Herzog designation of peaks (101, $10\bar{1}$) and (002), respectively.

TABLE IIIDIMENSIONS AND DENSITIES OF PELLETS

<u>Pellets</u>	<u>Diameter</u>	<u>Thickness(t)</u>	<u>Density(ρ)</u>
Cellulose Fibers	3.0 mm.	1.7 mm.	0.25 gm./cm. ³
Wiley-Milled Cellulose	3.0 mm.	0.5 mm.	0.85 gm./cm. ³
Ball-Milled Cellulose	3.0 mm.	0.4 mm.	1.06 gm./cm. ³

TABLE IVPROCEDURE FOR IRRADIATION OF SAMPLES

<u>Series</u>	<u>Samples</u>	<u>Pellets per Sample</u>	<u>Exposures per Pellet</u>	<u>Anode Voltage</u>	<u>Anode Current</u>	<u>Time of each Exposure</u>
1	F-1 to F-7	4	1	30 KV	20 mA	65 min.
2	M-1 to M-8	1	3	30 KV	$\approx$ 20 mA	45, 80, 100 min.
3	B-1 to B-12	1	3	30 KV	$\approx$ 20 mA	45, 80, 100 min.
4	H-0 to H-153	1	1	30 KV	$\approx$ 20 mA	$\approx$ 80 min.

Fig. 2. The maximum intensity of air scattering I_{as}^* , occurs at an angle $2\theta = 7^\circ 30'$.

Measurements of Absorption

Since sample F-6 contained entrapped benzene, measurements were made to determine any change in its X-ray absorption coefficient, using sample F-1 as a standard. In making absorption measurements the sample was alternately placed in position and removed, and two exposures at the same intensity were made of the nickel foil NN' (Fig. 1)*. From the difference in intensity of the (200) nickel interference the absorption $\mu_m \rho t$ of the sample was calculated using (18):-

$$\ln (I_{Ni})_{air} - \ln (I_{Ni})_{cell.} = \mu_m \rho t \quad \dots(1)$$

where

$(I_{Ni})_{cell.}, (I_{Ni})_{air}$ = Intensity of (200) nickel interference with and without sample in position respectively.

μ_m = Mass absorption coefficient of the sample ($\text{cm}^2/\text{gm}.$).

ρ = Packing density of the sample in gm./cm^3 .

t = Thickness of the sample in cm.

The resulting values of $\mu_{mp}t$ for samples F-1 and F-6, 0.383 and 0.363 respectively, agreed within experimental error indicating equal absorption coefficients. Hence, no correction was applied to the observed peak height of sample F-6; in Hermans' experiments such corrections were necessary (22).

Determination of Crystallinity Index

(i) Cellulose Fibers

Following the method of calculation used by Ant-Wuorinen (11), the per cent crystallinity index, X , is given by the following equation which is readily derived from Ant-Wuorinen's equations:-

$$X = \left[1 - \frac{80 \alpha}{I_{002} - I_{\text{Min.}}} \right] \times 100 \quad \dots(2)$$

where

I_{002} , $I_{\text{Min.}}$ and α^* are shown in Fig. 2

I_{002} = Height of A_4 peak in mm.

$I_{\text{Min.}}$ = Height of minimum point M above "zero" line in mm.

α = Width (MW) of peak A_4 in radians.

The conditions of irradiation for Series I, Table IV, produced a maximum intensity of air scattering, I_{as} , of 30 mm. and α was found to be independent of the intensity of irradiation. The results of the X-ray measurements for cellulose fibers are shown in Table V. Sample M-1 has been included for comparison.

(ii) Milled Cellulose Samples

For every sample in Series 2 and 3, Table IV, I_{as} was plotted against the corresponding values of I_{101} , I_{002} and I_{Min} . obtained from the photometer trace as in Fig. 2. Excellent straight lines of the type shown in Fig. 3 were obtained. The lines passed through the origin and the linearity was maintained up to an optical density of film blackening of 0.9*. The values at $I_{as} = 30$ mm. were obtained from the respective graphs* and X determined from equation 2. The same procedure was applied to samples exhibiting no interferences associated with crystallinity, except that the maximum intensity of the "amorphous" halo, I_{AmH} , was measured. Furthermore, the absence of the peaks A_4 and A_1 eliminated the minimum point M between them and α could not be measured.

The results of the X-ray measurements on the Wiley- and ball-milled cellulose are recorded in Table VI and VII, respectively.

TABLE V

RESULTS OF X-RAY AND HEATS OF WETTING EXPERIMENTS ON CELLULOSE FIBERS

Sample No.	Treatment	$\frac{A_1}{I_{101} \text{ mm.}}$	$\frac{A_4}{I_{002} \text{ mm.}}$	$\frac{I_{\text{Min.}}}{\text{mm.}}$	α radians	X %	Heat of Wetting Cal./gm.
F-1	Oven-dried at 105°C.	32.8(1.1)	48.8(2.1)	21.9(0.63)	0.0989	70.6(1.05)	13.06
F-2	Drying at room temperature over P ₂ O ₅ .	33.2(1.03)	49.0(2.2)	21.7(0.97)	0.0989	71.0(1.2)	13.90
F-3	Sample F-1, rewetted at room temperature and dried at 105°C (10 times).	32.0(1.3)	49.1(2.3)	20.0(0.53)	0.0989	72.8(1.5)	11.80
F-4	Sample F-2, rewetted and dried at room temperature over P ₂ O ₅ (10 times).	32.7(1.06)	48.0(2.4)	21.8(1.4)	0.0989	69.8(1.4)	12.98
F-5	Original wet sample freeze-dried.	33.6(1.2)	48.2(2.2)	22.5(1.1)	0.0989	69.2(1.4)	13.68
F-6	Original wet sample solvent-exchanged to and freeze-dried from benzene.	32.1(1.05)	44.2(1.7)	22.5(0.76)	0.0989	63.5(1.3)	11.98
F-7	Original wet sample, immersed in liquid nitrogen, allowed to melt and dried at room temperature over P ₂ O ₅ .	31.2(1.0)	44.3(1.9)	20.3(0.65)	0.0989	67.0(2.0)	13.46
M-1	Original wet sample dried at 105°C and Wiley-milled.	28.0	28.0	21.5	0.0817	0.00	17.40

Bracketed quantities denote standard deviations from the associated mean values.

TABLE VI
RESULTS OF X-RAY EXPERIMENTS ON WILEY-MILLED CELLULOSE

<u>Sample No.</u>	<u>Treatment</u>	$\frac{A_1}{I_{101}}$ <u>mm.</u>	$\frac{A_4}{I_{002}}$ <u>mm.</u>	$\frac{I_{Min.}}{mm.}$	α <u>radians</u>	χ <u>%</u>	K_{002} <u></u>
M-1	Original milled sample.	28.0	28.0	21.5	0.0817	0.00	0.934
M-2	M-1 water-wetted and dried.	30.0	37.0	21.0	0.0989	50.5	1.230
M-3	M-1 water-wetted and dried (10 times).	30.3	40.0	19.5	0.0989	61.4	1.330
M-4	M-1 immersed in ethanol and dried.	27.8	32.0	20.5	0.0946	33.8	1.065
M-5	M-1 immersed in ethanol and dried (10 times).	27.8	28.5	18.5	0.0903	28.7	0.956
M-6	M-1 immersed in acetone and dried.	29.4	29.5	22.5	0.0946	- ve	0.975
M-7	M-1 immersed in acetone and dried (10 times).	29.4	30.0	21.5	0.0903	15.0	1.018
M-8	M-1 exposed to water vapour at 93.3% R.H. and dried.	30.0	36.5	20.5	0.0989	50.5	1.200

TABLE VII
RESULTS OF X-RAY EXPERIMENTS ON BALL-MILLED CELLULOSE

<u>Sample No.</u>	<u>Treatment</u>	<u>A₁ I₁₀₁ mm.</u>	<u>A₄ I₀₀₂ mm.</u>	<u>I_{Min.} mm.</u>	<u>α radians</u>	<u>I_{AmH} mm.</u>	<u>X %</u>	<u>K₀₀₂</u>
B-1	Original milled sample.					28.5		
B-2	B-1 water-wetted and dried.	28.0	34.0	23.0	0.0989		28.0	1.115
B-3	B-1 water-wetted and dried (10 times).	27.5	35.0	21.0	0.0946		45.9	1.170
B-4	B-1 water-wetted and benzene dried.	26.0	31.5	22.5	0.0989		12.0	1.040
B-5	B-1 immersed in benzene and dried.					28.5		
B-6	B-1 immersed in ethanol and dried.					26.0		
B-7	B-1 immersed in ethanol and dried (10 times).					29.0		
B-8	B-1 immersed in acetone and dried.					28.0		
B-9	B-1 immersed in acetone and dried (10 times).					28.5		
B-10	B-1 immersed in methanol and dried.					28.5		
B-11	B-1 immersed in propanol and dried.					29.5		
B-12	B-1 immersed in butanol and dried.					27.5		

For Series 4, Table IV, the values of I_{101} , I_{021} , I_{002} , I_{Min} . and I_{AmH} , measured at the I_{as} of the exposure, were reduced to an $I_{as} = 30$ mm. by multiplying by the factor $30/\text{measured}(I_{as})$. The results of the X-ray experiments on the samples milled for progressive periods are recorded in Table VIII.

Value of K_{hkl}^* and Crystallinity

The ratio of a cellulose interference, I_{hkl} , and the intensity of a reference line of the Goppel (19) camera used by Hermans (18) yields a value independent of the energy of irradiation. A similar result is obtained if the Goppel interference is replaced by the maximum intensity of air scattering, I_{as} , occurring at an angle $2\theta = 7.30'$.

$$\text{Thus } \frac{I_{hkl}}{I_{as}} = K_{hkl} \quad \dots(3)$$

Any variation of I_{as} with atmospheric pressure was neglected.

In Table VI it is seen that in certain cases, although the diffraction pattern showed the unmistakable presence of A_1 and A_4 peaks, $\underline{X}$ failed to represent the state of crystallinity of samples subjected to severe mechanical degradation. In addition, the difficulty in measuring $\underline{\alpha}$ caused by the broadening of the minimum between the A_1 and

TABLE VIIIRESULTS OF X-RAY EXPERIMENTS ON CELLULOSEBALL-MILLED FOR PROGRESSIVE PERIODS

<u>Sample No.</u>	<u>A₁ I₁₀₁ mm.</u>	<u>I₀₂₁ mm.</u>	<u>A₄ I₀₀₂ mm.</u>	<u>I_{AmH} mm.</u>	<u>I_{Min.} mm.</u>	<u>α radians</u>	<u>X %</u>
H-0	32.2	29.2	45.1		22.1	0.0946	67.1
H-16	30.0	27.3	35.0		21.3	0.0946	44.8
H-32	31.0	28.4	32.3		23.7	0.0946	12.0
H-48	26.8	24.5	24.8		21.5	0.0903	
H-68	25.7	24.0	23.0		21.2	0.0860	
H-80	26.2		23.4	25.6	23.4	0.0860	
H-96	25.8			26.1	24.2		
H-114	25.7			26.2	24.8		
H-132	26.8			28.7	26.8		
H-153				28.5	25.6		

A_4 peaks, introduces an error of $(0.16 \text{ to } 0.20)\underline{X}$, when $\underline{X}$ is in the range 20 to 30%. Since the A_4 peak is more sensitive to crystallinity changes than A_1 , the value of $\underline{K_{002}}$ may provide a parameter which is less susceptible to error and which is capable of continuously representing the state of crystallinity of cellulose. Assuming approximately equal size distribution of crystallites, $\underline{I_{002}}$ for a given $\underline{I_{as}}$ will be greater for a more crystalline than for a less crystalline sample.

In Tables VI and VII, $\underline{K_{002}}$ was determined from the slope of the straight lines obtained by plotting $\underline{I_{as}}$ vs. $\underline{I_{002}}$. Fig. 3 shows the plot of $\underline{I_{002}}$ vs. $\underline{I_{as}}$ of four cellulose samples of different degrees of crystallinity. Dewaxed cotton linters, a cellulose of high crystallinity which is estimated from various methods to amount to 70% (22), was included for comparison. $\underline{I_{002}}$, $\underline{X}$ at $(\underline{I_{as}})30$ and $\underline{K_{002}}$ are given in Table IX. Fig. 3 and Table IX show that $\underline{K_{002}}$ decreases together with $\underline{X}$, and in addition, gives a positive value in the case of sample M-1 where $\underline{X}$ misleadingly indicates the total destruction of crystallinity.

Heats of Wetting

Heats of wetting by liquid water were measured for samples F-1 to F-7 and M-1 using a Bunsen isothermal calorimeter with diphenyl ether as the working substance (23).

FIGURE 3

GRAPH SHOWING VARIATION OF INTENSITY OF (002) PEAK
WITH CRYSTALLINITY OF CELLULOSE AND MAXIMUM INTENSITY
OF AIR SCATTERING

- 1 = Dewaxed cotton linters.
- 2 = Sample F-7.
- 3 = Sample M-2.
- 4 = Sample M-1.

TABLE IX

VARIATION OF I_{002} , X AND K_{002}
WITH
DEGREE OF CRYSTALLINITY

<u>No.</u>	<u>Sample</u>	$\frac{A_4}{I_{002}}$ <u>mm.</u>	X <u>%</u>	<u>K_{002}</u>
1	Dewaxed Cotton Linters	58.5	79.8	1.950
2	F-7	44.3	67.0	1.535
3	M-2	37.0	50.5	1.230
4	M-1	28.0	0.0	0.934

The apparatus was kept in a thermostat maintained at $26.90 \pm 0.003^\circ\text{C}$. The results of these experiments are shown in Table V.

Differential Staining*

Differential staining of fibers provides a visual and qualitative means of demonstrating variations in the density of amorphous cellulose and the degree of fibrillation (24). Samples F-1 to F-7 were dyed with a solution of equal parts of Benzo-Fast Yellow A and Benzo Brilliant Blue 6BS. The dyes were obtained from Farbenfabriken, Leverkusen, Germany. The technique used by Jayme (25) was followed in its entirety. The results of the differential staining experiments are shown in Fig. 4.

Measurements of Viscosity

To follow the effect of mechanical degradation on the degree of polymerization (D.P.), viscosity measurements were made on samples F-1 and M-1 and H-0 to H-153. The viscosity pipet procedure described in Tappi method T-230 sm-50 was followed in its entirety.

The intrinsic viscosities were calculated from Schulz and Blaschke's (26) equation:-

$$\eta_{sp}/c = [\eta](1 + k'\eta_{sp}) \quad \dots(4)$$

FIGURE 4DIFFERENCES IN COLOURATION OF FIBERS WITH DRYING METHOD

(a) Wet (virgin) pulp.

(b) Sample F-1.

(c) Sample F-5.

(d) Sample F-6.

(a), (b), (c) and (d) taken at
a magnification 100X.

(e) From left to right:-

1. Sample F-2.

2. Sample F-4.

3. Wet (virgin) pulp.

4. Sample F-3.

5. Sample F-5.

6. Sample F-7.

7. Sample F-6.

8. Sample F-1.

(a)

(b)

(e)

(d)

(c)

where

η_{sp} = Specific viscosity.

c = Concentration of cellulose in gm./dl.

k' = $2.303k$.

k = 0.13 (Martin's (27) constant).

$[\eta]$ = Intrinsic viscosity in dl./gm.

The degree of polymerization was calculated from the equation (28):-

$$\text{D.P.} = 156[\eta] \quad \dots(5)$$

The intrinsic viscosities and D.P. values are recorded in Table X.

TABLE X

VARIATION OF THE DEGREE OF POLYMERIZATION OF CELLULOSE
WITH MECHANICAL DEGRADATION

<u>Sample No.</u>	<u>$[\eta]$ dl./gm.</u>	<u>D.P.</u>
F-1	2.70	422
M-1	2.49	389
H-0	4.83	755
H-16	2.68	418
H-32	2.57	402
H-48	2.41	376
H-68	2.24	350
H-80	2.08	325
H-96	1.94	303
H-114	1.79	279
H-132	1.62	253
H-153	1.53	239

Cellulose Fibers

From Table V it is seen that drying cellulose fibers under different conditions produces little change in the crystallinity index, $\underline{X}$. Although the diffraction pattern of fibers dried by evaporation of water and freeze-drying remains unaltered, the heats of wetting vary with the method of drying. Only for sample F-6 could a change in $\underline{X}$ be detected.

The results obtained for samples F-1 to F-4 and F-7, suggest that any relative changes in crystallinity, which may arise from variations in intra-fiber bonding with the method of drying, are small compared with other changes tending to decrease the accessibility, as indicated by the heats of wetting. Since the quantity of heat evolved when cellulose is wetted with water is believed to be primarily due to an interaction of the water molecules with free hydroxyl groups of the cellulose, it may be taken as a measure of the accessibility of these hydroxyl groups (29). On this assumption, it may be inferred that in conformity with previous findings, the hornified^{*} (2) regions and "junction"^{*} (30) points established with a first drying in samples F-1 and F-2 increase with repeated wetting-drying cycles (samples F-3 and F-4) as well as with the temperature of drying. The formation of impenetrable vitreous regions

* Terms marked with an asterisk are defined in Appendix I.

and "junction" points would then immobilize and prevent the interaction of any available hydroxyl groups with the water molecules without necessarily increasing lateral order.

Freezing the fibers as in sample F-7 may be assumed to have reduced their hydrophilic (31) character and to have produced the same effect on the accessibility as drying at a temperature between 105°C and room temperature. In freeze-drying cellulose fibers the plasticizing action of water is reduced and the mobility of the molecular chains curtailed. In addition, previous work has shown that freeze-drying decreases the tendency of bond formation, and this tendency is reduced in the absence of hemicellulosic^{*} material (5, 6). From the comparable heat of wetting values for the samples dried by evaporation of water and sample F-5, it may be assumed that hemicelluloses prevent a substantial reduction in intra-fiber bonding. For sample F-6, benzene being a poor swelling and a poor hydrogen bonding medium, it may be reasonable to conclude that the degree of alignment of the molecular chains in the amorphous region during drying from benzene is less than with water. Hence, any additional crystallization produced in this manner in drying from water will be absent with benzene-dried fibers. Fibers dried in this manner would

be expected to have a lower $\underline{X}$ and a higher value of heat of wetting than fibers dried by evaporation of water. However, since sample F-6 contained trapped benzene, the heat of wetting of 11.98 cal./gm. is of doubtful validity.

An attempt was made to determine $\underline{X}$ by taking a diffraction diagram of the wet (virgin) fibers, but it proved unsuccessful because it was not possible to make a quantitative separation of the scattering due to water from that due to cellulose.

Fig. 4 shows the effect of different drying procedures on the staining of cellulose fibers. The colour differences resulting from the staining procedure depends upon the dyeing properties of the different components of the dyes. The main component of the yellow dye has a greater affinity for cellulose than either component of the blue dye, but the blue dye is composed of smaller molecules than the yellow dye. Hence, the blue dye can enter a capillary network into which the yellow dye, in spite of its greater affinity for cellulose, is not admitted (25). A cellulose structure having fine capillaries will be dyed blue to blue-green, while a structure in which the molecular chains are less highly bonded would stain yellow.

In the virgin (a) as well as the solvent-exchanged

sample (d), intra-fiber bonding was at a minimum and a yellow colouration resulted. In contrast, the highly bonded fibers resulting from the evaporation of water, acquired a similar blue to blue-green colouration exhibited by the oven-dried sample (b). The colour of the freeze-dried sample (c) further indicated that drying by sublimation of water reduced intra-fiber bonding to a smaller extent than drying by solvent exchange.

The shades in colouration become more distinct when the stained fibers are viewed in bulk as in Fig. 4(e). The most striking differences in colouration are again exhibited by the undried (virgin) and solvent-exchanged samples No. 3 and 7, respectively. Fibers dried by room-temperature evaporation of water stained pale green (No. 1) and the colouration did not intensify when the fibers were stained after having been wetted and dried ten times (No. 2). Fibers dried by evaporation of water at 105°C stained pale blue (No. 8), while fibers which had been wetted at room temperature and dried at 105°C exhibited a more intense blue colouration upon staining (No. 4). Freeze-drying (No. 5) or treatment with liquid nitrogen (No. 6) resulted in greenish-yellow fibers upon staining.

From these results it could be inferred that intra-fiber bonding is at a minimum in the undried (virgin) pulp sample and at a maximum in sample F-3 (No. 4).

Milled Cellulose

From Tables V, VI and VII it is seen that Wiley-milling increases the heat of wetting of cellulose fibers and reduces $\underline{X}$ to zero, while ball-milling destroys the crystallinity. Figs. 5, 6 and 7 are reproductions of photometer traces of X-ray diffraction patterns of F-1, M-1 and M-2, B-1, B-2 and B-4, and B-1 (in the dry and wet state), respectively. By comparing Fig. 5(b) with 5(a), the following points may be noted:-

- (1) Wiley-milling reduces the intensity of the A_1 and A_4 peaks;
- (2) The grinding action preferentially destroys the $A_4(002)$ planes, reducing the A_4 peak intensity to 57% of its value in F-1, while the A_1 peak suffers a reduction of only 20%;
- (3) The width α in M-1, a measure of the crystallite* size, is also reduced.

In contrast, the X-ray diffraction pattern of B-1 showed only a diffuse halo which can be seen in Fig. 6(a) as a broad maximum in the region previously occupied by the (021) peak.

Treatment of the milled material with water

resulted in the following behaviour:-

- (1) Partial restoration of crystallinity, Figs. 5(c) and 6(b);
- (2) Exposure of the Wiley-milled product to water vapour at 93.3% R.H. resulted in the same degree of recrystallization as for M-2;
- (3) Repeated wetting and drying (samples M-3 and B-3) further increased $\bar{X}$;
- (4) Recrystallization of B-1 occurred in the wet state, Figs. 7(a) and 7(b);
- (5) Displacing the water from the wetted ball-milled sample with benzene and drying from the non-polar solvent resulted in a smaller degree of recrystallization than with B-2, Fig. 6(c);
- (6) No modification to cellulose II occurred, but a slight shift was observed in the position of the A_4 peak of the treated ball-milled samples.

Treatment of the Wiley-milled samples with organic liquids gave smaller $\bar{X}$ values than with water. Because of the large error associated with such small

FIGURE 5RADIAL PHOTOMETER TRACES OF X-RAY DIFFRACTION PATTERNS OF
CELLULOSE FIBERS AND WILEY-MILLED CELLULOSE

- (a) Sample F-1.
- (b) Sample M-1.
- (c) Sample M-2.

FIGURE 6RADIAL PHOTOMETER TRACES OF X-RAY DIFFRACTION PATTERNS OF
BALL-MILLED CELLULOSE

- (a) Sample B-1.
- (b) Sample B-2.
- (c) Sample B-4.

Fig. 5

Fig. 6

FIGURE 7

RADIAL PHOTOMETER TRACES OF X-RAY DIFFRACTION PATTERNS OF
DRY AND WET BALL-MILLED CELLULOSE

(a) Sample B-1 - dry.

(b) Sample B-1 - wet.

(b)

(a)

values of $\bar{X}$, the state of crystallinity can be better appreciated by referring to the K_{002} values. It is seen that wetting with ethanol once gives, as expected from its greater swelling power, a larger K_{002} value than acetone. Anomalously, a lower K_{002} value was obtained for repeated wetting and drying from ethanol than for a similar treatment using acetone, but this may have been due to contamination of the acetone with water. In contrast, treatment of the ball-milled samples with organic liquids produced no detectable X-ray interferences associated with crystallinity.

The increase in the heat of wetting of sample M-1 may be readily explained by an increase in the number of available hydroxyl groups. The disruption of the hydrogen-bonded crystalline lattice and the reduction in the degree of polymerization of the fibers with grinding (Table X) exposed hitherto unavailable hydroxyl groups which could then react with the water molecules. Although a reduction in the size of the crystallites would be expected to produce an increase in the width α of the A_4 peak in sample M-1, the observed decrease may be attributed to a change in the distribution of the crystallite size; the larger crystallites surviving the destructive action better than the smaller ones. The progressive

decrease in α with milling, observed in Table VIII, is at present inexplicable.

In order to explain the recrystallization of the milled material with water it may be assumed that mechanical degradation, in destroying the crystalline regions, also ruptures the junctions restraining normal swelling of the fibers. The plasticizing action of water, by conferring mobility on the chains, allows their realignment and the surface tension of water during drying promotes hydrogen-bonding which increases the lateral order. Repeated wetting and drying would be expected to further extend the process of realignment and a higher degree of lateral order attained.

The identical results obtained for samples M-2 and M-8 may indicate that removal of the water in the earlier stages of drying contributes little to recrystallization. Upon addition of water beyond the range of "bound" water the rapid rise in the sorption isotherm in the high humidity regions cannot be explained by assuming formation of new sorption sites by swelling. In the opinion of various workers, water in the high relative humidity regions is adsorbed as multilayers^{*}(32) or, by capillary condensation^{*}(33) or, by solution^{*} of the non-crystalline cellulose (34).

Such water will condense within the structure with heat effects associated with normal condensation (35, 36). However, since only imbibed* water can affect the intrinsic properties of the fibers and promote their rearrangement, it is reasonable to assume that recrystallization of M-8 had occurred in the range of 60 - 70% R.H.

Broughton and Wang (10), investigating the strength of handsheets dried from non-aqueous liquids, observed a similar behaviour. Upon conditioning butanol-dried handsheets to water vapour of 85% R.H., the strength attained was found to be as great as that of a sheet initially formed from water. These authors do not discount the possibility of an increase in bonding occurring only at the onset of capillary condensation. According to Barkas (37), such condensation begins at a relative humidity of 65 - 70%.

By comparing values of α for the undegraded and milled material, it may be inferred that the "mending" action of water reproduces the same distribution of crystallite size existing before degradation. The low $\bar{X}$ and K_{002} values obtained for sample B-4 fall within expectation. Here, as in sample F-6, the mobility of the chains in benzene is greatly curtailed and there is

little tendency for hydrogen-bonding. Consequently, the resulting material will have a low degree of lateral order. These results further confirm previous findings that drying from benzene is more efficacious in preventing bond formation in fibers than drying by sublimation of water (10).

Stamm and Tarkow (16) found that the swelling power of the normal alcohols for cellulose and wood decreased progressively with ascent of the homologous series. In general, these workers found that the extent of penetration and swelling of cellulosic materials by organic liquids depends upon the ability of the liquid to promote hydrogen-bonding. Furthermore, swelling depends upon the polarity and molecular volume of the liquids. This is illustrated by the inability of di-n-butylamine and tri-n-butylamine, which show a large tendency to form hydrogen-bonds with hydroxyl groups, to produce the same pronounced swelling with cellulose as n-butylamine. Furthermore, in spite of the comparable hydrogen-bonding tendencies of the normal alcohols from methyl to amyl alcohol, their sorption by cellulose differs appreciably. This behaviour has been attributed to steric hindrance which prevents the larger swelling molecules from approaching sufficiently close to the immobile hydroxyl groups of

cellulose (16).

The results obtained for sample M-4 to M-7 are generally consistent with the idea that the amount of recrystallization occurring on drying increases with the swelling capacity of the liquid. As expected, ethanol produced a higher lateral order in the degraded fibers than acetone, but less than for water. From the results of the ball-milled samples treated separately with benzene and acetone, it may be safely concluded that no recrystallization is possible with these liquids. The almost complete absence of order in the ball-milled samples, and the smaller swelling capacities for cellulose of the alcohols with respect to water, may be responsible for the incapability of these media to produce any detectable recrystallization. Here, it may be assumed that the relatively weaker swelling medium is unable to align the molecular chains without the initial presence of well defined crystallites to act as anchoring points.

Although in this case the presence of "nuclei" of ordered regions appears to be indispensable for recrystallization, a further tentative deduction may be drawn from the variations in the intensity of the amorphous halo I_{AmH} , for the alcohol-treated samples. However, before discussing this possibility the results in Table VIII

must be examined.

Fig. 8 is a reproduction of photometer traces of X-ray diffraction patterns of H-0, H-32, H-68, H-96 and H-132. From the traces and Table VIII, the following observations may be made:-

- (1) The A_4 peak diminishes steadily and disappears after 80 hours of milling;
- (2) The (021) peak also diminishes and disappears between 68 and 80 hours of milling, being replaced by an amorphous* halo;
- (3) The position of the maximum intensity of the amorphous halo coincides with the position of the (021) peak it has replaced;
- (4) The intensity of the amorphous halo increases and finally levels out after 132 hours of milling;
- (5) The A_1 peak resists initial degradation and begins to suffer only after 32 hours of milling;
- (6) Table VIII shows that the intensity of $I_{\text{Min.}}$ increases with decreasing crystallinity

FIGURE 8

RADIAL PHOTOMETER TRACES OF X-RAY DIFFRACTION PATTERNS OF
CELLULOSE BALL-MILLED FOR PROGRESSIVE PERIODS

- (a) Sample H-0.
- (b) Sample H-32.
- (c) Sample H-68.
- (d) Sample H-96.
- (e) Sample H-132.

(c)

(b)

(a)

(e)

(d)

and hence may be taken as a measure of the amorphous content;

- (7) The increasing intensity of I_{Min} helps to maintain constant the intensity of the A_1 peak which merges with the background after 132 hours of milling.

Fig. 9 shows a plot of the intensity of the (021) peak against time of milling. The curve has a minimum region where the transition from the (021) peak to the amorphous halo takes place. The intensity of the (021) peak decreases gradually with milling until, after 70 hours, the intensity of the amorphous halo predominates and increases with continued milling. After approximately 130 hours, it reaches its final value of 28.5 mm. This stage appears to mark the limiting effect of the grinding process, for although the sample is not completely amorphous, the intensity of the "amorphous" halo remains constant with further milling.

By referring to Fig. 9 and having regard to the hydrogen-bonding tendencies of the different alcoholic media, variations in I_{AmH} may be taken to herald the beginnings of the (021) lattice planes of cellulose I. Thus, since the alcohols are known to engage in hydrogen-bonding, the I_{AmH}

FIGURE 9

GRAPH SHOWING VARIATION IN INTENSITY OF (021) PEAK
WITH TIME OF BALL-MILLING

$$\bigcirc = I_{021}$$

$$\triangle = I_{AmH}$$

values for the ethanol- and methanol-treated samples may be considered to be I_{021} values on the left of the transition region in Fig. 9. For the propanol- and butanol-treated samples, the assumption must be made that steric hindrance bars these molecules from penetrating into the degraded cellulosic structure and no (021) lattice planes are formed. Although the evidence is inconclusive, the formation of the (021) lattice planes under these conditions should not be necessarily discounted.

SUMMARY AND CONCLUSIONS

Cellulose Fibers

Variations in the degree of intra-fiber bonding resulting from drying undried virgin pulp by different methods produces no relative change in crystallinity, except when freeze-dried from benzene when a slightly lower value for the crystallinity index was obtained. It was concluded that benzene, being a non-supporter of hydrogen-bonding and a poor plasticizer for cellulose, prevents intra-fiber bonding to an even higher extent than freeze-drying, and a lower degree of lateral order results on drying from benzene than from water. Heats of wetting indicated that "hornification" was increased by repeated wetting and drying and with increased temperature of drying. Freezing of cellulose fibers before drying by evaporation of liquid water reduces their hydrophilic character. Entrapped benzene in the fibers dried by solvent exchange renders the heat of wetting value inconclusive.

Differential staining of fibers further confirmed that bonding is at a minimum in the undried virgin pulp as well as the solvent-exchanged sample. On the other hand, evaporation of liquid water and the presence of hemi-celluloses during freeze-drying produces a higher degree of

intra-fiber bonding.

Milled Cellulose

The destruction of the crystallites and decrease in the degree of polymerization with mechanical degradation increases the number of available hydroxyl groups and, consequently, the heat of wetting. In addition, Wiley-milling destroys preferentially both the A_4 planes and the smaller crystallites. During recrystallization of the milled material, the powerful plasticizing action of water confers mobility on the molecular chains and provides an opportunity for realignment. Hydrogen-bonding on drying is further promoted by the surface tension of water and a higher lateral order ensues. Cyclic wetting and drying further extends the ordered regions. Since only imbibed water can promote the rearrangement of the fibers, the recrystallization of the Wiley-milled material, exposed to water vapour at 93.3% R.H., is attributed to imbibition. As with the undegraded fibers, the feeble swelling capacity of benzene is held responsible for the lower degree of lateral order resulting in drying ball-milled pulp by solvent exchange. The higher swelling capacity of ethanol for cellulose produces a higher lateral order in the Wiley-milled pulp than acetone. The failure of the alcohols to produce

any detectable recrystallization with the ball-milled material has been attributed to their lower swelling capacity than water. In order that such liquids may be capable of producing any realignment of the degraded fibers, the initial presence of ordered regions, to act as anchoring points for the molecular chains, appears to be essential. The suggestion has also been made that methanol and ethanol may be capable of reproducing to a limited extent the (021) lattice planes of the ball-milled material, whilst steric hindrance prevents propanol and butanol from establishing such order.

SUGGESTIONS FOR FURTHER WORK

Innumerable suggestions could be made for pursuing the present investigations. A few of the ones likely to yield immediate results are mentioned here.

- (1) The effect on the crystallinity index of freeze-drying cellulose fibers from water containing a surface tension depressant could be determined;
- (2) The Wiley-milled fibers studied in this work were ground at a blade clearance of 3×10^{-3} in. The destructive effect on the crystallinity of fibers ground for various periods and at different blade clearances could be investigated. Finding a blade clearance which would allow the fibers to be "fluffed" without reducing their crystallinity would greatly facilitate the formation of pellets for exposure to X-rays;
- (3) The recrystallization of Wiley-milled fibers by various swelling media, including the strongly swelling amines, may lead to interesting results;

- (4) Following the evidence of recrystallization of Wiley-milled pulp fibers by conditioning at high relative humidity (R.H.), milled material could be conditioned at various R.H. and its crystallinity index determined;
- (5) In addition, since heats of wetting and sorption ratios are a measure of lateral order, an attempt to correlate these values either with the crystallinity index or K_{hkl} values might prove successful;
- (6) In the milling of cellulose material, Bachman (38) maintains that ultrasonic frequencies are responsible for the destruction of the crystallites and the degradation of wood constituents in general. This theory could be verified by comparing the relative degradation wrought by ball-milling and ultrasonic treatment of the fibers. The degradation could be determined by X-rays or viscosity measurements;
- (7) The grinding process may be followed by X-ray low angle scattering measurements. Information regarding particle size may be

obtained by following the angular displacement of half the maximum intensity value of the scattering. Furthermore, the X-ray low angle scattering absorption coefficient could be determined. This coefficient is directly proportional to the particle size;

(8) Finally, further developments should be made of methods -

- (i) for determining the X-ray crystallinity of cellulose in the presence of water (39), and
- (ii) capable of giving absolute values of the crystallinity in cellulose fibers. The present method, developed by Hermans (18) suffers from the uncertainty involved in separating the diffraction due to the ordered regions from that of the amorphous portion of cellulose.

APPENDIX IGLOSSARY OF TERMS IN INTRODUCTION AND DISCUSSION

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APPENDIX IGLOSSARY OF TERMS IN INTRODUCTION AND DISCUSSIONACCESSIBILITY

The functional groups of cellulose capable of reacting with certain reagents are the hydroxyl groups of the glucose residues. In the crystalline regions, the hydroxyl groups are engaged in inter-bonding the molecular chains by hydrogen bridges and are, therefore, inaccessible to reagents. On the surface of the crystallites and in the amorphous regions, the hydroxyl groups are not engaged in cross-linking the molecular chains and are available for reaction. The fraction of total cellulose which can react with certain reagents under specified conditions represents its accessibility. The accessibility of a given cellulose is not unique but depends upon the reagent and the swelling medium in which the reaction takes place.

Some of the chemical methods used for determining the accessibility are hydrolysis (40), thallation (41), oxidation (7) and formylation (42). Physical methods include density measurements (43), deuterium exchange (44), water sorption (45), heats of wetting (29) and X-ray

diffraction (18). Unlike the destructive chemical methods, physical methods used for accessibility determinations leave the sample intact.

"BOUND" WATER

Water which is adsorbed by hydrogen-bond formation with unbonded hydroxyl groups of cellulose fibers is said to be "bound" water (46). This water is bound to the cellulose with a greater bonding energy than normally found for water, and its bonding is accompanied by evolution of heat above that of normal condensation.

CELLULOSE

(i) Occurrence

Cellulose is claimed to be the most abundant of all naturally occurring organic compounds, and probably accounts for at least one-third of all the vegetable matter in the world. It is the principal constituent of cell-walls of the higher plants in which it forms the structural framework. The most important sources of cellulose are wood, cotton, leaf fibers, bast fibers, grasses, straws and agricultural residues. Naturally occurring cellulose is

also known as native cellulose or Cellulose I.

(ii) Molecular Structure

Cellulose is a polysaccharide. Its chain-like molecules are composed of polymerized anhydro D-glucopyranose residues, in the "chair" form, joined to one another by 1:4 β -linkages. Its degree of polymerization may attain 3000 - 5000 glucose units corresponding to a molecular weight of 300,000 - 500,000 (47). The length of such molecules has been estimated from X-ray photographs to be 15,000 - 20,000 Å (48). Fig. 1 (a) represents the modern view of the constitution of cellulose.

(iii) Crystalline and Amorphous Regions of Cellulose

Cellulose fibers are made up of chain molecules of cellulose held together laterally by intermolecular forces. The monomer units in one chain are joined with one another by means of primary valencies. In certain regions of the fibers, the molecular chains are parallel to one another and maximum three-dimensional order results. These regions are known as crystallites. They form the crystalline portion of cellulose and give sharp X-ray diffraction patterns. The amorphous portion of cellulose, which gives diffuse X-ray diffraction patterns, is made up

of regions in which the molecular chains are arranged haphazardly.

The boundary between the crystalline and amorphous regions of cellulose is not sharp; instead, there is a gradation of order, and an amorphous region must be considered as possessing all possible intermediate degrees of order, from completely amorphous to perfectly crystalline. The relative amount of amorphous and crystalline cellulose, although constant for one sample, varies with the origin of cellulose, e.g. cotton is 70% crystalline while the crystallinity of regenerated fibers is only 40%.

(iv) Crystal Structure of Cellulose I

Fig. 1 (b) shows the unit cell structure of Cellulose I (49). The repeating unit in the monoclinic elementary cell in the direction of the axis b , is the cellobiose unit. Each corner, as well as the center, is occupied by a cellulose chain whose glucose residues are pointing alternately in opposite directions, with the center chain running anti-parallel to the other four.

Three different forces hold the lattice together. The glucose units of the cellulose molecule are bound together by primary valency bonds running parallel to the

b axis. In the a direction of the unit cell the molecules are held together by hydrogen-bonds, and in the c direction van der Waal's forces are operative.

The bond energies in the three directions are also indicated in calories. By comparing these lattice forces, it can be readily seen why cellulose swells more along the c direction, laterally, in preference to the a direction where hydrogen bonds must first be disrupted before any swelling can occur, and not at all longitudinally.

(v) Cellulose II

Transformation of the crystalline lattice of Cellulose I by the action of 18% sodium hydroxide (mercerization), concentrated solutions of acids and certain salts results in a product termed Cellulose II. The fibrous structure is retained and the axes of the monoclinic unit cell have the following dimensions (50):-

$$\begin{aligned} a &= 8.14 \text{ \AA} \\ b &= 10.3 \text{ \AA} \\ c &= 9.14 \text{ \AA} \\ \beta &= 62^\circ \end{aligned}$$

Fig. 1 (c) gives a view down the b axis of the unit cell

FIGURE 1MOLECULAR AND CRYSTAL STRUCTURE OF CELLULOSE

- (a) Molecular structure of cellulose.
(30), p. 8
- (b) Unit cell structure of cellulose.
(McBain, J.W., "Colloid Science",
D.C. Heath and Co., Boston (1950),
p. 313.).
- (c) View down b axis of the unit cell
of Native (Cellulose I) and
Mercerized (Cellulose II) Cellulose
(ibid. p. 314.).

(a)

(b)

(c)

of native (Cellulose I) and mercerized (Cellulose II) cellulose.

CRYSTALLINITY INDEX

In the determination of absolute values of the crystallinity in cellulose by X-ray diffraction (18), an immediate difficulty is the separation of the diffraction due to the crystalline portion from that due to the amorphous portion. Although the crystallinity index (11) is only an indirect measure of crystallinity, it can be readily obtained from the X-ray diffraction pattern of cellulose, and is based on the following facts:-

- (1) Increasing amorphous content of cellulose broadens the X-ray diffraction rings;
- (2) Increasing crystallinity increases the optical density of these rings.

By measuring the width and intensity of the main diffraction ring A_4 , and forming a ratio of these quantities as described in Section 2, equation 2, a useful parameter, indicating the state of crystallinity of a cellulose sample, may be obtained.

DRYING

Freeze-drying

The process by which a wet product is frozen and (in the case of water) the ice removed by sublimation under vacuum is known as "freeze-drying".

This method of desiccation has found many useful applications, especially with heat-sensitive medicinal and food products (51). One important difference between drying by evaporation of liquid water and freeze-drying is the elimination of the compressive effect of the surface tension of water upon freezing. As a result, particles of freeze-dried pulverized products have little tendency to agglomerate, and the dried powders flow freely. With fibrous materials such as cellulose, the elimination of the surface tension of water during drying greatly reduces inter-fiber bonding, and the resulting material is bulkier than if the fibers had been dried by evaporation of water.

Solvent Exchange

The drying of cellulose fibers by "solvent exchange" is conducted in two stages:-

- (1) The water is replaced by a miscible and polar organic liquid such as acetone,

methanol or ethanol;

- (2) The polar organic liquid is in turn replaced by a miscible but non-polar organic liquid such as benzene.

The net effect is that the water is replaced by a larger polar molecule and the hydroxyl groups, distributed along the cellulose chains, have less chance to interact with one another when the large homopolar molecules of benzene are removed by isothermal evaporation.

The disadvantage in this method lies in the great retentive capacity of the fibers for the organic liquid which is still entrapped by the fibers at the end of the dehydration (17, 52).

HEMICELLULOSES

Hemicelluloses (53) are polysaccharides of lower degree of polymerization than cellulose. They are found in the mature cell wall of plants, and form part of the system interpenetrating and incrusting the cellulosic fabric. They are insoluble in water and more readily hydrolyzed by dilute mineral acids than cellulose. The polysaccharide chains may be composed of xylose or mannose residues and the accompanying sugar units of the polyuronide

hemicelluloses may be either hexoses or pentoses.

HORNIFICATION

The term "hornification" is used to denote the structural changes, accompanying the drying of cellulose fibers, which reduce the capacity of cellulose to reabsorb water and affect its accessibility adversely.

The formation of hornified regions is attributed to the presence of hemicelluloses in the larger pore spaces of the amorphous regions. Upon drying, through the interaction of cohesive and adhesive forces, the regions enclosing the molecular chains of cellulose assume a greater density of packing resulting from a contraction of the pores and the disappearance of capillaries. Such regions, although amorphous in character, are impenetrable to liquids.

HYDROGEN

Hydrogen-bonding

The ability of hydrogen to link electronegative elements of small atomic radius enables it to form a bridge known as a "hydrogen-bond". The lateral joining of contiguous molecular chains is effected through their

respective hydroxyl groups by hydrogen-bonding. For every link so established, the hydrogen atom of one is joined to the oxygen atom of another hydroxyl group. Hydrogen-bonds $\text{-OH} \cdots \text{O-}$ belong to the category of secondary valency forces and have an energy value of 5000 - 8000 calories per mole (54).

"JUNCTION" POINTS

The points at which a network of individual chain molecules of cellulose cohere are known as "junction" points. In the amorphous regions the chains are arranged in a haphazard criss-crossing manner, and the junction points are scattered throughout the network. However, relatively short sections of these chains may be parallel to one another and be held together by hydrogen-bonds. Although such regions may possess the high order prevailing in a crystalline lattice, they may be too small to give rise to sharp X-ray interferences, and hence cannot be rightfully classed as crystalline. On the other hand, they act as crystalline regions towards water absorption and restrict the swelling of cellulose.

LATERAL ORDER

The structure of cellulose fibers has been broadly subdivided into "crystalline" and "amorphous" regions. In addition, it is now generally assumed that a whole spectrum of order exists between complete order and disorder (55). A high degree of lateral order is associated with a region possessing repeating atomic planes along the three co-ordinate axes. It has a definite density and produces a sharp X-ray diffraction pattern. Regions with diminishing degrees of lateral order will have repeating distances along either two or one axis, and finally the chains may be only approximately parallel to one another. Lateral order is closely related to the degree of hydrogen-bonding. A statistical measure of lateral order for a small volume V is given by (56):-

$$\bar{O} = [\text{OH}_c] / [\text{OH}_t]$$

where

- $\bar{O}$ = Degree of order.
- $[\text{OH}_c]$ = Number of hydrogen-bonds in volume V .
- $[\text{OH}_t]$ = Total possible number of hydrogen-bonds if all the molecules are perfectly crystallized.

SORPTION OF WATER BY CELLULOSE

The first water sorbed by dry cellulose fibers is bound by the hydroxyl groups of the molecular chains in the form of a hydrate. Upon addition of more water beyond the range of hydrate formation, the swelling which occurs may be regarded as a local dissolution of molecular chains in the amorphous regions. Water which has entered the fiber in this manner is for convenience called "imbibed" water (57).

In the region between 20 to 80% R.H. the adsorption agrees with the polymolecular theory and the water is assumed to be added in multilayers (58).

In the region above 80% R.H. it is assumed that the water condenses in the spaces between the fibers and is known as "capillary" water.

APPENDIX IIADDITIONAL DETAILS OF EXPERIMENTAL PROCEDURES AND RESULTS

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APPENDIX II

ADDITIONAL DETAILS OF EXPERIMENTAL PROCEDURES AND RESULTS

GENERAL

The X-Ray Camera

Fig. 1 (a) shows the assembled camera. The nickel foil and supporting frame can be seen between the collimating system on the left and the film-supporting plate on the right. The beam-stop, shown mounted between the nickel foil and the back-plate, was not used.

Fig. 1 (b) shows the camera mounted on the X-ray tube. The enveloping black cloth served to protect the film from light during an exposure to X-rays.

Preparation of Fibers for Pelleting

A prime requisite in making comparative X-ray measurements is to maintain constant the mass and the geometrical shape of the irradiated samples.

As mentioned in Section 2, isotropic packing in the plane of the holder was ensured by laboriously disentangling the fibers from the thickly matted samples by means of two dissecting needles. In this manner, isolated regions of densely packed fibers were eliminated and

FIGURE 1

THE X-RAY CAMERA

- (a) Assembled X-ray camera.
- (b) Camera mounted on X-ray tube and enveloped in black light-tight cloth.

(a)

(b)

irradiation of the pellets produced diffraction rings with circumjacent points of uniform optical density of blackening (within experimental error).

The Sample Holder and Pellet Press

Fig. 2 and 3 show the sample holder and the different parts of the pellet press, respectively.

The sample holder can be fitted onto the base of the press as well as the collimating system of the camera. In position on the base, it can be loaded to a depth of 1.93 mm. With a primary beam 1 mm. in diameter, the diffracted rays from the principal planes of Cellulose I and II emerge unobstructed by the rim of the loading chamber.

The press shown in Fig. 3 consists of five separate parts: base, body, sleeve, plunger and spacer.

With the sample holder in position, the top of the base-pillar is 1.93 mm. from the face of the loading chamber of the sample holder. When the parts are assembled without the spacer, the plunger protrudes into the empty loading chamber of the sample holder, and is in contact with the base-pillar.

To form the pellet the sample holder was placed on the base and small quantities of the loose fibers added until a weight of 3 mg. $\pm$ 3% was attained. The press

FIGURE 2

THE SAMPLE HOLDER

SAMPLE HOLDER

SCALE: 1:4 (mm)

FIGURE 3

THE PELLET PRESS

PELLET PRESS

SCALE: 1:2 (mm)

PLUNGER

BODY

SLEEVE

LEGEND:
 — STAINLESS
 STEEL
 --- BRASS

BASE

SPACER

was then assembled and the fibers compressed by placing the press in a vise for 30 minutes. The 1.3 mm. spacer, interposed between the head of the plunger and the body of the press, enabled each sample to be compressed to the same volume. Transmission of the whole compressive force to the pellet was ensured by having the body of the press resting on the shoulders of the sample holder. The sleeve prevented tilting of the body during compression.

Although no binding material was used, the pellet retained its shape indefinitely, even after ejecting it from the holder.

The preparation of pellets of the milled pulp was much simpler than with whole fibers. Scraping was unnecessary, and for 3 mg. pellets the spacer was not used. Gentle pressure on the plunger was sufficient to bind firmly the pulverized material.

Conditions of Developing and Processing of Films

The X-ray films were developed under the following conditions:-

Film: Ilford-B Industrial X-ray film;

Developer: Ilford ID - 19;

Fixing Solution: Ilford IF - 9;

Stop Bath: 180 cc. of 28% Glacial Acetic Acid
per gallon of water;

Temperature of Developing and "Fixing": 20°C;

Time of Developing: 5 minutes;

Time of "Fixing": 5 minutes;

Washing: One hour in running water at 20°C;

Drying: Air-dried at room temperature.

MEASUREMENTS OF INTENSITY

The Densitometer

In this instrument a beam of light of small scanning area is focussed on the film which lies on a stage capable of travelling across the beam. The transmitted beam is in turn brought to a focus on a slit in front of a photocell.

In its excursion over the diffraction pattern the incident beam traverses regions of varying optical density. The modified intensities of the transmitted light fall upon the photocell, and the voltage fluctuations after amplification are relayed to a moving coil galvanometer.

A lens system focusses another beam of light on the mirror affixed to the galvanometer coil and the reflected beam is made to pass through a slit onto a photographic paper. The photographic paper is housed in a cassette geared to the stage supporting the X-ray film, and

a continuous photometer curve is thus obtained. The selection of a suitable transmission ratio (1, 2, 4, 6, 40) determines the horizontal travel of the photographic paper relative to the stage and enables small areas of the diffraction pattern to be scrutinized in great detail.

A "Sola" constant-voltage transformer stabilized the voltage and the intensity of the incident beam was further stabilized by a split-beam arrangement incorporated in the instrument.

Intensity of Diffraction Rings

A diffraction pattern of pulp fibers, in which the crystallites are randomly oriented should, in theory, give smooth rings of uniform intensity around their entire circumference. In practice such uniformity is not attained unless the film is rotated during an exposure. When an exposure is made with a stationary film, the following factors may combine to destroy this uniformity:-

- (1) Inhomogeneity in the cross-sectional intensity of the primary beam;
- (2) Inhomogeneity of the fiber pellets;
- (3) Obliquity of the primary beam with respect to the film;
- (4) Non-uniformity of the film emulsion;

- (5) Non-uniform distribution of density in the black paper protecting the film from light.

Factor No. (5) was eliminated by enveloping the camera in a light tight black cloth and leaving the film bare during an exposure.

To compensate for the other causes, eight radial photometer traces, at 45° intervals, were taken of each diffraction pattern. By this means the heights of eight peaks could be measured for each diffraction ring, and the mean value of the peak heights was taken as representing the intensity of the particular ring.

In the present investigation, the method used for measuring the degree of crystallinity does not require a complete radial trace for each interval. It is sufficient to scan only that region of the diffraction pattern originating from the principal diffracting planes of cellulose, and the region of maximum intensity of air scattering.

Fig. 4 is a reproduction of eight radial photometer traces (transmission ratio 1:2) taken at 45° intervals, of the principal interferences on a diffraction pattern of a pellet of whole cellulose fibers.

The mean values of $\underline{I_{002}}(A_4)$, $\underline{I_{101}}(A_1)$, $\underline{I_{Min}}$. and

FIGURE 4

RADIAL PHOTOMETER TRACES, TAKEN AT 45° INTERVALS.
OF A₁ AND A₄ INTERFERENCES ON AN X-RAY DIFFRACTION PATTERN
OF CELLULOSE FIBERS

MW determined from Fig. 4 are:-

$$I_{002} = 50.5 \text{ mm.}$$

$$I_{101} = 33.1 \text{ mm.}$$

$$I_{\text{Min.}} = 20.0 \text{ mm.}$$

$$\text{MW} = 12.0 \text{ mm.}$$

The mean value of I_{as} on the same diffraction pattern is found in a similar manner.

Miller Indices

To define the positions in space of parallel lattice planes in a crystal, a system of reference coordinates has been developed by Miller.

Three non-coplanar directions $\underline{X}$, $\underline{Y}$, $\underline{Z}$, in the crystal are chosen and these termed crystallographic axes. The origin of the axes is placed at the center of the crystal and the crystal planes are indexed in terms of their intercepts upon the axes. Along each axis a unit distance is chosen and the distances from the origin of the given plane along the three axes measured; the reciprocals of these intercepts are then the Miller indices of the plane. Thus, a plane intersecting the $\underline{X}$ axis at unit distance from the origin and parallel to the $\underline{Y}$ and $\underline{Z}$ axes has the intercepts $1, \infty, \infty$ and the indices are written (100).

Air Scattering

A portion of the energy in the primary beam is dissipated by scattering from the gas molecules of the air. Fig. 5 is a reproduction of a photometer trace of a diffraction pattern of air. Because of the almost complete absence of order in a gaseous scattering medium, the angular distribution of this scattered energy is continuous, being largest at small angles. The maximum intensity of air scattering I_{as} occurs at an angle of $7^{\circ}30'$.

MEASUREMENTS OF ABSORPTION

The Nickel Foil

In making absorption measurements, the frame of the nickel foil intercepted all cellulose scattering making an angle $2\theta > 27^{\circ}50'$. Hence, the (200) nickel interference fell on a film region free of cellulose interferences.

Fig. 6 shows a composite diffraction pattern of the principal interferences A_1 and A_4 of Cellulose I and the (111) and (200) interferences of nickel.

For any sample the intensity of a ray diffracted at sufficiently small angles is given by (59):-

$$I = ktI_0 e^{-\mu_m t} \quad \dots(1)$$

FIGURE 5RADIAL PHOTOMETER TRACE OF AN X-RAY DIFFRACTION PATTERN
OF AIR SCATTERING

I_{as} = Maximum intensity of air scattering.

FIGURE 6

COMPOSITE X-RAY DIFFRACTION PATTERN OF CELLULOSE AND NICKEL

(200), (111) = Nickel interferences.

A_4 , A_1 = Cellulose Interferences.

FIGURE 7

RADIAL PHOTOMETER TRACE OF FIGURE 6

Fig. 6

Fig. 7

where

$$\begin{aligned} I_0 &= \text{Intensity of primary beam;} \\ I &= \text{Intensity of diffracted ray;} \\ k &= \text{Constant.} \end{aligned}$$

μ_m , ρ and t have the same significance as in equation (1),
Section 2.

With no sample in position:-

$$I_{(Ni)air} = kt'I_0 e^{-\mu'_m \rho' t'} \quad \dots(2)$$

where

μ'_m , ρ' and t' refer to nickel.

With the cellulose sample in position, the
incident beam suffers an additional absorption. Hence:-

$$I_{(Ni)cellulose} = kt'I_0 e^{-\mu'_m \rho' t'} e^{-\mu_m \rho t} \quad \dots(3)$$

where

μ_m , ρ and t refer to cellulose.

Equations (2) and (3) may be combined to give:-

$$\ln(I_{Ni})_{air} - \ln(I_{Ni})_{cellulose} = \mu_m \rho t \quad \dots(4)$$

Compton Scattering

Compton or incoherent scattering takes place when an incident photon strikes an electron, and part of the radiation is transmitted at a longer wave length than the primary radiation (60).

The increase in wave length is given by:-

$$\Delta\lambda = \frac{2h}{mc} \sin^2 \phi/2 \quad \dots(5)$$

where

$$\begin{aligned} h &= \text{Planck's constant} = 6.6254 \times 10^{-27} \text{ erg.sec.} \\ m &= \text{Electron rest mass} = 9.1086 \times 10^{-28} \text{ gm.} \\ c &= \text{Velocity of light} = 2.9979 \times 10^{10} \text{ cm.sec.}^{-1} \\ \phi &= \text{Angle between direction of scattered photon} \\ &\quad \text{and incident photon.} \end{aligned}$$

When an exposure of cellulose is made with the nickel foil in position, the Compton scattering of the nickel is superimposed on that of cellulose. At normal intensities of exposure the resulting background in the region of the cellulose interferences (Fig. 6) becomes too dense and distorts the photometer trace of the A_1 and A_4 peaks. Fig. 7, a reproduction of the photometer trace of Fig. 6, clearly illustrates the "swallowing" up of the peaks A_1 and A_4 . On such a trace, the intensity of the

(200) nickel peak only can be measured.

Compton scattering in the region of the cellulose interferences can be eliminated by intercepting the primary beam after its emergence from the nickel foil by means of a beam-stop. However, this device eliminates air scattering as well. In aligning the beam-stop with the primary beam, care should be taken to prevent the rim of the beam-stop from projecting into the cone of the (200) nickel interferences. The minimum permissible distance of separation of the beam-stop from the nickel foil can be calculated from the diameter of the beam-stop and the angle of diffraction of the (200) nickel interference ($51^{\circ}36'$).

DETERMINATION OF CRYSTALLINITY INDEX

The Determination of α

To express any horizontal distance MW mm. on a photometer trace in radians, it is necessary to know the angle γ subtended at the center of the sample by the corresponding distance on the diffraction pattern.

To determine γ , a diffraction pattern of a carbon pellet was taken, and the diameter of its well defined $3.35\text{\AA}$ interference ring was measured on the photometer trace, taken at a transmission ratio 1:4.

From the Bragg equation (61):-

$$n\lambda = 2d\sin\theta \quad \dots(6)$$

where

λ = Wave length of X-rays = $1.54 \text{ \AA}$;

d = Interplanar distance of diffracting planes = $3.35 \text{ \AA}$;

θ = Angle, in degrees the incident beam makes with the diffracting planes;

$n = 1$.

θ was found to be $13^\circ 17'$. Hence:-

$$2\theta = \gamma = 26^\circ 34'.$$

Diameter of $3.35 \text{ \AA}$ diffraction ring = 218 mm .

Radius of $3.35 \text{ \AA}$ diffraction ring = 109 mm .

The number of radians δ per millimeter of horizontal length on a photometer trace taken at a transmission ratio 1:4 is given by:-

$$\begin{aligned} \delta &= \frac{\pi \times 26^\circ 34'}{180 \times 109} \\ &= 0.0043 \text{ rad./mm.} \end{aligned}$$

For any other transmission ratio r , δ is given by:-

$$\delta = \frac{0.0043 \times 4}{r}$$

$$= \frac{0.0172}{r} \text{ rad./mm.} \quad \dots(7)$$

Therefore, α is given by:-

$$\alpha = \int \text{MW rad.} \quad \dots(8)$$

Optical Density of X-ray Film

The degree of blackening or optical density caused by X-rays impinging on a film is given as the fraction $\underline{T}$ of an incident light beam which it transmits.

The density $\underline{D}$ is given in terms of the transparency $\underline{T}$ by (62):-

$$\begin{aligned} D &= \text{Log} \frac{1}{T} \\ &= \text{Log} \frac{\text{Incident light}}{\text{Transmitted light}} \quad \dots(9) \end{aligned}$$

The density of any point on the diffraction pattern can be calculated from the corresponding point on the photometer trace; e.g. the density of the point $\underline{M}$ in Fig. 2, Section 2, is given by:-

$$D = \text{Log} \frac{80}{80 - I_{\text{Min.}}} \quad \dots(10)$$

Since the final 10 mm. of galvanometer deflection correspond to an increase in density of 0.9 to infinity, the ability of the densitometer to follow variations in optical density above 0.9 decreases very rapidly. Most X-ray films are

sensitive to a density of blackening of 3.0 before they become "saturated".

In taking exposures, therefore, the intensity should be adjusted so that the densest region on the diffraction pattern does not exceed a density of 0.9. This density is equivalent to a galvanometer deflection of 70 mm. on the scale.

Intensity of Cellulose Peaks and Air Scattering

Fig. 8 shows a typical graph obtained by plotting I_{101} , I_{002} and $I_{Min.}$ vs. I_{as} . The present graph was obtained for sample M-2 and the values of I_{101} , I_{002} and $I_{Min.}$ at $I_{as} = 30$ mm. are 30.0, 37.0 and 21.0, respectively. Similar graphs were obtained with samples M-1 to M-8 and B-1 to B-12.

VALUE OF K_{hkl} AND CRYSTALLINITY

The Determination of K_{hkl}

The following considerations led to the formation of equation (3), Section 2:-

- (1) The cellulose samples irradiated had always the same weight and geometrical shape.
Hence, the attenuation of the primary beam,

FIGURE 8

GRAPH SHOWING THE VARIATION IN INTENSITY OF

I_{101} , I_{002} AND $I_{Min.}$ WITH I_{as}

- at the same energy of irradiation,
would be constant for all samples;
- (2) Compton scattering was assumed to be constant for all samples (18);
 - (3) The amorphous scattering of cellulose in the region of maximum air scattering ($2\theta = 7^{\circ}30'$) was assumed to be negligible compared with the intensity of air scattering;
 - (4) No diffraction lines of cellulose are known to occur in the region of $2\theta = 7^{\circ}30'$ (63);
 - (5) The poor resolution of the camera ($16.6 \text{ \AA}$) excludes low-angle scattering in the region $7^{\circ}30'$;
 - (6) No scattering from the beam-exit pin-hole was detected;
 - (7) All exposures were made at room temperature. Any variations in the intensity of air scattering with atmospheric pressure was neglected.

For cellulose, the intensity I_{hkl} of a ray diffracted at sufficiently small angles is given by equation (1).

Remembering that the incident beam suffers

absorption by the cellulose, the intensity of air scattering I_{as} , at an angle $2\theta = 7^\circ 30'$, is given by:-

$$I_{as} = k'' t'' I_0 e^{-\mu_m'' \ell'' t''} e^{-\mu_m \ell t} \quad \dots(11)$$

where

μ_m'' and ℓ'' refer to air.

k'' = Constant;

t'' = Effective thickness (cm.) of air traversed by the incident beam.

The quantities μ_m , ℓ and t for cellulose and air remain constant and the system is invariant. Hence, for a given sample, substituting I_{hkl} for I in equation (1) and combining equations (1) and (11) gives:-

$$\frac{I_{hkl}}{I_{as}} = K_{hkl} \quad \dots(12)$$

K_{hkl} is a constant for the diffracting plane having Miller indices hkl , and is independent of the energy of exposure. Such a constant can be found for any point on the diffraction pattern.

BIBLIOGRAPHY

1. Corte, H. and Schaschek, H., Das Papier, 9, 519 (1955).
2. Jayme, G., Cellulosechem., 21, 73 (1943).
3. Jayme, G., Papier Fabrik, 42, 187 (1944).
4. Assaf, A. G., Haas, R. H. and Purves, C. B., J. Am. Chem. Soc., 66, 66 (1944).
5. Van den Akker, J. A., Tappi, 35, 13 (1952).
6. Marchessault, R. H., Lodge, W. C. and Mason, S. G., Svensk Papperstidn., 59, 859 (1956).
7. Goldfinger, G., Mark, H. and Siggia, S., Ind. Eng. Chem., 35, 1083 (1943).
8. Conrad, C. G. and Scroggie, A. G., Ind. Eng. Chem., 37, 592 (1945).
9. Brown, R. K. and Purves, C. B., Pulp and Paper Mag. Can., 48(6), 100 (1947).
10. Broughton, G. and Wang, J. P., Tappi, 38, 412 (1955).
11. Ant-Wuorinen, O., Paperi ja Puu, 37, 335 (1955).
12. Hess, K., Kiessig, H. and Gundermann, J., Z. Physik. Chem., 49, 64 (1941).
13. Hermans, P. H. and Weidinger, A., J. Am. Chem. Soc., 68, 2547 (1946).
14. Kanamaru, K. and Chao, J., Kolloid-Z., 84, 85 (1938).
15. Lauer, K., Kolloid-Z., 107, 86 (1944).
16. Stamm, A. J. and Tarkow, H., J. Phys. and Colloid Chem., 54, 745 (1950).
17. Marchessault, R. H., McKnight, T. S. and Mason, S. G., to be published.

18. Hermans, P. H. and Weidinger, A., J. App. Phys.,
19, 491 (1948).
19. Goppel, J. M. and Arlman, J. J., App. Sci. Res.,
A1, 3 (1947).
20. Mark, H., "Physik und Chemie der Cellulose", Julius
Springer, Berlin (1932), p. 140.
21. Clark, G. L., "Applied X-Rays", McGraw-Hill Book Co.,
Inc., New York (1955), Chap. 13.
22. Hermans, P. H. and Weidinger, A., J. Polym. Sci.,
4, 135 (1949).
23. Screaton, R. M. and Mason, S. G., Svensk Papperstidn.,
60, 379 (1957).
24. Simons, F. L., Tappi, 33, 312 (1950).
25. Jayme, G. and Harders-Steinhäuser, M., Das Papier,
9, 507 (1955).
26. Schulz, G. V. and Blascke, F., J. Prakt. Chem.,
158, 130 (1941).
27. Davis, W. E. and Elliott, J. H., in Ott, E. and
Spurlin, H. M., "Cellulose and Cellulose Derivatives",
Interscience Publishers, Inc., New York (1955),
Part III, p. 1217.
28. Immergut, E. H., Rånby, B. G. and Mark, H. F., Ind.
Eng. Chem., 45, 2482 (1953).
29. Rees, H. W., J. Text. Inst., 39, T351 (1948).
30. Hermans, P. H., "Physics and Chemistry of Cellulose
Fibers", Elsevier Publishing Co., Inc., New York (1949),
p. 189.
31. Klenkova, N. I., J. App. Chem., U.S.S.R., 27, 401 (1954),
Eng. Trans.
32. Brunauer, S., Emmett, P. H., Teller, E., J. Am. Chem. Soc.,
60, 309 (1938).

33. Preston, J. M., Nimkar, M. V. and Gundavda, S. P.,
J. Text. Inst., 42, T79 (1951).
34. Hermans, P. H., "Physics and Chemistry of Cellulose
Fibers", Elsevier Publishing Co., Inc., New York (1949),
Part II, Chap. 2 and 6, Part III, Chap. 8.
35. Smith, S. E., J. Am. Chem. Soc., 69, 646 (1947).
36. Magne, F. C., Portas, H. J. and Wakeham, H., J. Am.
Chem. Soc., 69, 1896 (1947).
37. Barkas, W. W., "The Mechanical Properties of Wood and
Their Relation to Moisture", Interscience Publishers,
Inc., New York (1953), pp. 54 - 56.
38. Bachmann, D., Z. Ver. deut. Ing., Verfahrenstech.,
No. 2, 43 (1940).
39. Hermans, P. H. and Weidinger, A., Die Makromolekulare
Chemie, 18/19, pp. 75 - 81 (1956).
40. Nickerson, R. F. and Habrle, J. A., Ind. Eng. Chem.,
39, 1507 (1947).
41. Assaf, A. F., Haas, R. H. and Purves, C. B., J. Am. Chem.
Soc., 70, 877 (1948).
42. Nickerson, R. F., J. Text. Res., 21, 195 (1951).
43. Hermans, P. H., "Physics and Chemistry of Cellulose
Fibers", Elsevier Publishing Co., Inc., New York (1949),
p. 200.
44. Mann, J. and Marrinan, H. J., Trans. Faraday Soc.,
52, 487 (1956).
45. Howsmon, J. A., J. Text. Res., 19, 152 (1949).
46. Howsmon, J. A., in Ott, E. and Spurlin, H. M., "Cellulose
and Cellulose Derivatives", Interscience Publishers,
Inc., New York (1954), Part I, p. 396.
47. Mark, H., Amer.-Scientist, 31, 104 (1943).
48. Rånby, B. G., Tappi, 35, 53 (1952).

49. Gross, S. T. and Clark, G. L., Z-Krist., 99, 357 (1938).
50. Andress, K. R., Z. Physik. Chem., 34, 190 (1929).
51. Flosdorf, E. W., "Freeze-Drying", Reinhold Publishing Corp., New York (1949).
52. Magne, F. C. and Skau, E. L., J. Text. Res., 22, 748 (1952).
53. Norman, A. G., in Ott, E. and Spurlin, H. M., "Cellulose and Cellulose Derivatives", Interscience Publishers, Inc., New York (1954), Part I, Chap. 5B.
54. Huggins, M. L., J. Org. Chem., 1, 407 (1936).
55. Baker, W. O., Fuller, C. S. and Pape, N. R., J. Am. Chem. Soc., 64, 776 (1942).
56. Howsmon, J. A. and Sisson, W. A., in Ott, E. and Spurlin, H. M., "Cellulose and Cellulose Derivatives", Interscience Publishers, Inc., New York (1954), Part I, pp. 251 - 255.
57. Preston, J. M., Nimkar, M. V. and Gundavda, S. P., J. Text. Inst., 42, T79 (1951).
58. Babbitt, J. B., Can. J. Res., 20A, 143 (1942).
59. Klug, H. P. and Alexander, L. E., "X-Ray Diffraction Procedures", John Wiley and Sons, Inc., New York (1954), p. 205.
60. Clark, G. L., "Applied X-Rays", McGraw-Hill Book Co., Inc., New York (1955), p. 168.
61. Bragg, W. L., Proc. Camb. Phil. Soc., 17, 43 (1912).
62. Klug, H. P. and Alexander, L. E., "X-Ray Diffraction Procedures", John Wiley and Sons, Inc., New York (1954), p. 108.
63. Mark H., "Physik und Chemie der Cellulose", Julius Springer, Berlin (1932), pp. 154 - 5.