[COMMUNICATION NO. 35 FROM THE LABORATORY FOR CELLULOSE RESEARCH OF THE AKU AND AFFILIATED COMPANIES]

On the Recrystallization of Amorphous Cellulose

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1. Preparation of Amorphous Cellulose by Grinding.—In a paper dealing with the treatment of native cellulose fibers in a vibrating ball mill Hess, Kiessig and Gundermann[1] reported that the X-ray diagram characteristic of the fibers soon disappeared; the crystalline interferences faded and were replaced by a broad amorphous ring, indicating that the crystalline lattice was destroyed by the mechanical impact of the balls on the fiber.

Microscopic examination reveals two characteristic types of mechanical disintegration products. First, the fibers show a marked fibrillation into finest fibrils and secondly numerous particles without clearly recognizable structure appear. The latter will be designated as "cellulose powder." Both products can be observed shortly after the beginning of the grinding operation, but, as the latter proceeds, microscopically visible fiber fragments more and more disappear and the powder becomes predominant. The fibrous fragments still show a crystalline X-ray pattern, the powder does not.

Examination with the electron microscope (EM) reveals the occurrence of fine fibrils admixed with the powder. The fineness of the fibrils extends itself far beyond the resolving power of the light microscope. According to Hess, *et al.*, elementary fibrils of 70–130 Å. diameter preformed in the original fiber appear as the final disintegration product. This statement could not be confirmed by Husemann.[2] Hess, *et al.*, have only published one single picture of elementary fibrils from wood pulp fibers and according to Husemann this picture must be ascribed to some kind of impurity in Hess' preparations and is by no means characteristic of the wood fiber. According to Husemann no lower limit of fibril size is observed and no morphologically very characteristic products are obtained when the fibers are milled in the dry condition. As will be shown below, we ourselves have not found any indication of preformed elementary fibrils in ramie and other fibers. The diameter of the fibrils seems to assume any size down to the limit of the resolving power of the instrument used.

The powder particles seem to consist of loose agglomerations of a cellulose component and porcelain grindings from the balls and the walls of the mill. It is difficult to disclose the morphological structure of the cellulose component, but X-ray photographs of the powder reveal that it must occur in a non-crystalline condition.

It is not the aim of this paper to enter into much detail on the morphology of the grinding products and we shall merely consider them as a source of amorphous cellulose. We shall confine ourselves to reproducing some characteristic micrographs of the grinding products. In Figs. 1–4 some low magnification pictures taken with an ordinary microscope are given. Figure 1 shows the fibrillation in ramie fibers, Fig. 2 the "powder" obtained from ramie after two hours of milling, suspended in water. In Fig. 3 the grinding product of rayon after one hour of milling is reproduced, showing unchanged fragments of rayon filaments and "powder." Finally, Fig. 4 shows the "powder" from wood pulp fibers after four hours of milling (all suspended in water).

It should be remarked that the dimensions of the powder particles depend on the manner in

Fig. 1.—Fibrillation in ramie fibers after milling (stained with iodine–zinc chloride; mag. 64 ×).

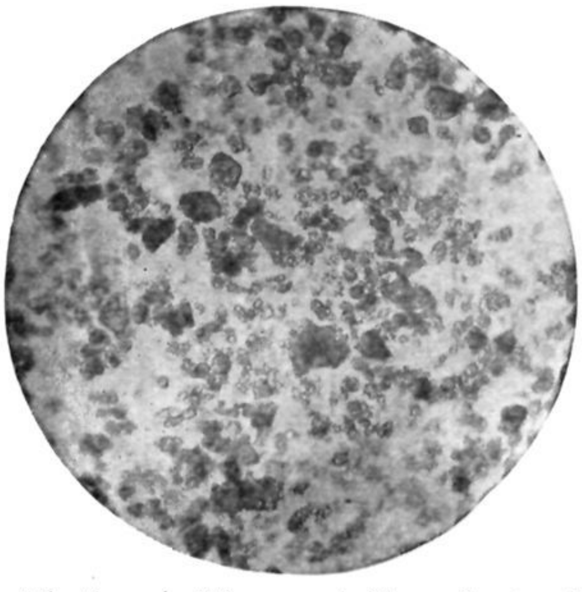

Fig. 2.—The "powder" from ramie fibers after two hours of milling (suspended in water; mag. 64 ×).

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(1) K. Hess, H. Kiessig and J. Gundermann, *Z. physik. Chem.*, **B49**, 64 (1941).

(2) E. Husemann, *J. makrom. Chem.*, **1**, 158 (1943).

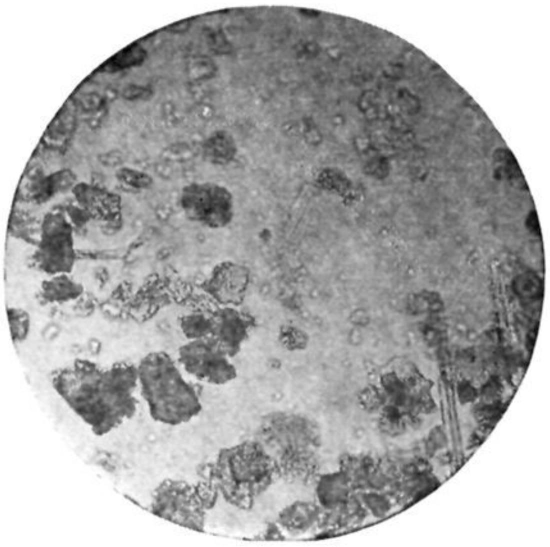

Fig. 3.—The "powder" from rayon after one hour of milling, suspended in water (fiber fragments still present); mag. 64 ×.

which the microscopic preparations are made. On wetting the powder with water, the particles become finer when rubbed or stirred with the water or if the cover glass is moved to and fro several times. The cellulose powder so obtained is readily soluble in 1 N sodium hydroxide. When introducing this reagent under the cover glass the particles disappear to leave only a cloudy suspension of very fine porcelain particles. The resulting solution is viscous. Apparently the solubility of the cellulose is very much enhanced after the destruction of the crystalline order. In Fig. 4a the dissolution of the powder from wood pulp upon introduction of 1 N sodium hydroxide under the cover glass in one half of the field of vision is shown with low magnification.

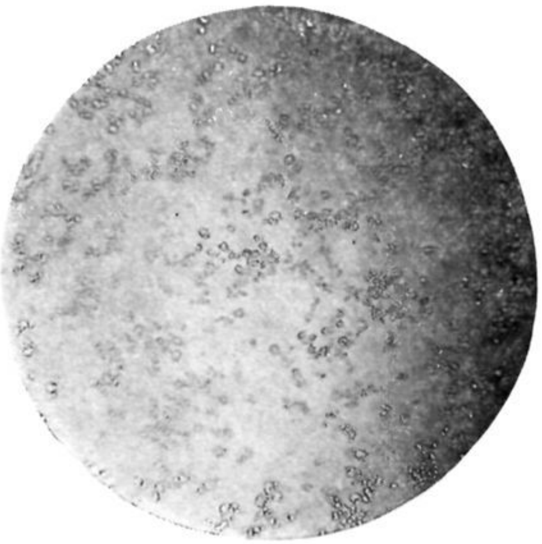

Fig. 4.—The "powder" from woodpulp fibers after four hours of milling suspended in water; mag. 64 ×.

Figure 5 is an electron micrograph of a preparation from ramie powder. It shows porcelain particles (large black fragments) admixed with fibrillar elements of a very irregular shape, which represent the cellulose component. After a long search some of the latter elements, relatively free from porcelain particles, could be detected and photographed at large magnification (Figs. 6 and 7).

Fig. 4a.—Powder from wood pulp (ground five hours) dissolving in sodium hydroxide; mag. 20 ×.

It would seem that the cellulosic component of the powder consists of crumpled and otherwise deformed but still fibrillar elements.

In milling the fibers, care was taken that the material was very dry initially and remained dry during the grinding operation (Hess, *et al.*, do not indicate in their paper whether they operated with very dry or with air-dry material).

2. Recrystallization of the Amorphous Cellulose.—Hess, Kiessig and Gundermann have found that the amorphous grinding product recrystallized on heating with water, yielding the X-ray pattern of cellulose II (hydrate cellulose). They claim that a good diagram of cellulose II is only obtained after long grinding and that, after shorter times of grinding, a portion of the material recrystallizes to give cellulose I (native modification). According to our own investigations it would seem that this statement is incorrect and that the interferences of cellulose I observed are due to admixture of unchanged fiber fragments or fibrils from the original material, which can hardly be separated from the powder when taking the samples. Moreover, the percentage of fibrous material in the sample depends on the method of sampling. In order to get a clear picture of the effect of the recrystallization in water, one and the same sample should be photographed before and after the transformation, and the authors do not indicate whether they followed this procedure.

We have enclosed samples of the "powder," as free from fibrous fragments as possible, in a thin-walled capillary. After an X-ray photograph was taken, the contents of the capillary were wetted with water by introducing a drop of water into the capillary. Then the latter was sealed, heated to 100° and reopened. After the contents had been allowed to dry, a second X-ray photograph was taken of the same sample.

The X-ray photographs were taken with a comparison camera of the type introduced by Astbury, allowing of exposing two objects alternately for intervals of a few minutes to the same

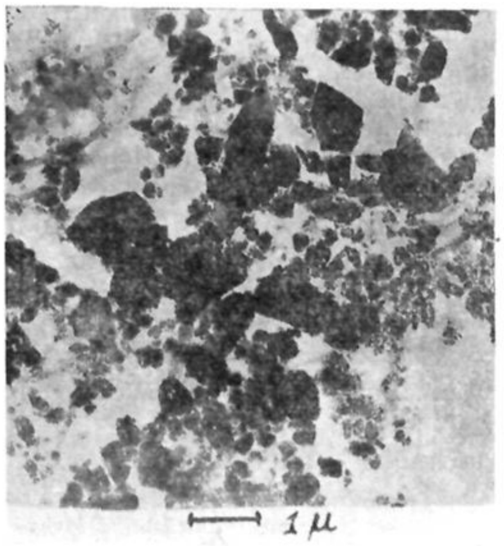

Fig. 5.—Mag. 7000 ×.

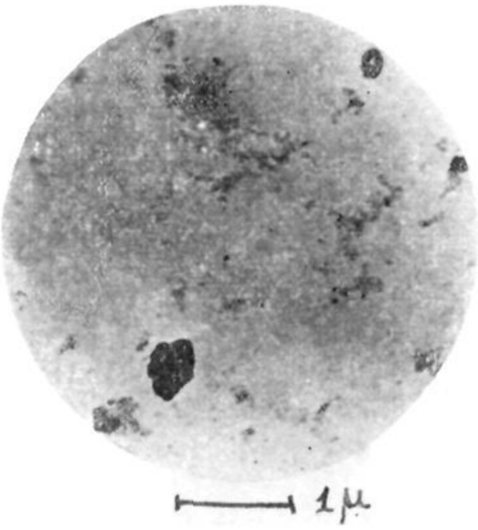

Fig. 6.—Mag. 11000 ×.

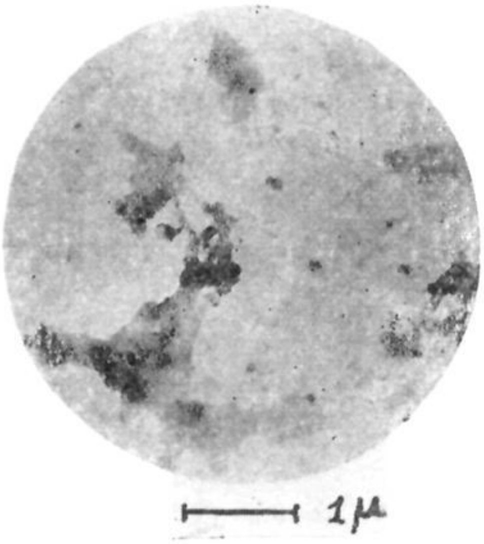

Fig. 7.—Mag. 11000 ×.

Electron micrographs of ramie powder after one hour of dry milling.

pencil of X-rays, thus making sure that both preparations receive the same amount of radiation. The diagrams obtained with the capillaries containing the cellulose samples were compared with those of an empty capillary having approximately the same size and wall thickness, in order to get also a photograph of the radiation scattered by the glass capillary and by the air in the camera.

X-Ray photographs of typical samples of ramie powder so obtained before and after heating with water are reproduced in Figs. 8 and 9. (Two quadrants in each photograph represent the X-ray pattern of the capillary with the sample and the other two quadrants that of the empty capillary.) The photographs were photometered in a radial direction in the cellulose and in the comparison quadrants. Subtraction gives the intensity of the radiation diffracted by the cellulose powder itself. The result is shown in Fig. 10a for the powder before recrystallization and in Fig. 10b after recrystallization. The peaks indicated by P are interferences due to the porcelain grindings with which the preparations were contaminated. They occur in both Fig. 10a and Fig. 10b. Figure 10a shows only a faint indication of the presence of the most intense interference A_4 of native cellulose, which lies between A_3 and A_4 of regenerated cellulose (indicated by arrows on the top of the figure), whereas in Fig. 10b the normal pattern of crystalline cellulose II is visible, including the A_0 interference. The background of diffusely scattered radiation, obtained by subtracting the crystalline peaks from the total intensity distribution is indicated by dotted lines.

In order to reach a quantitative comparison of the intensity distributions before and after recrystallization the ordinates of the curves in Figs. 10a and 10b were multiplied by a factor, so chosen that the intensity of the diffraction at high angles relative to the incident beam became equal. This procedure serves to reduce both observations to

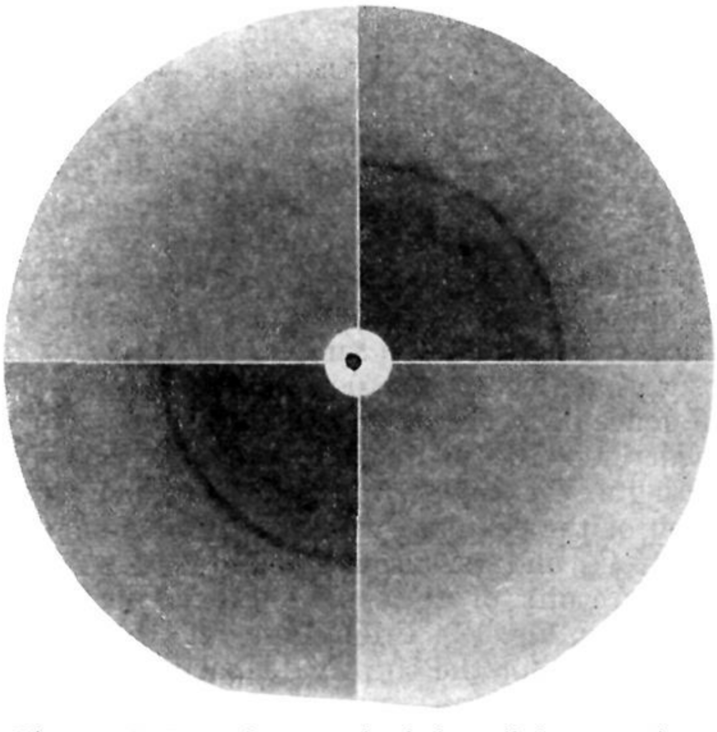

Fig. 8.—X-Ray photograph of the cellulose powder.

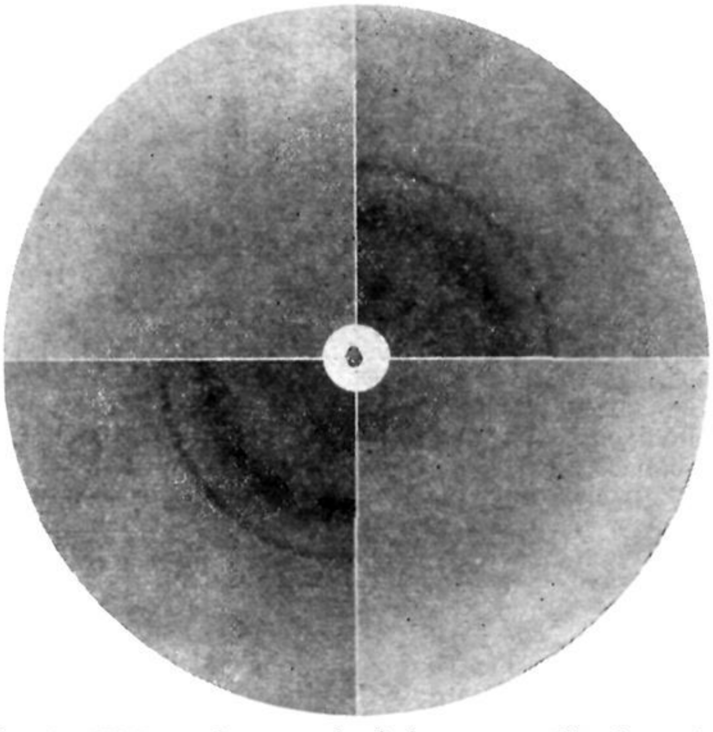

Fig. 9.—X-Ray photograph of the recrystallized powder.

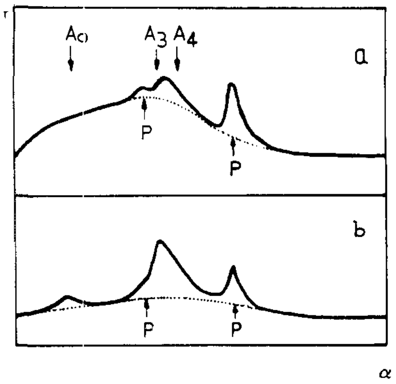

Fig. 10.—Radial intensity distribution in the X-ray photographs of dry cellulose powder (a) before and (b) after recrystallization, derived from radial photometer curves of the diagrams shown in Fig. 8 and Fig. 9 after subtraction of the scattering due to the glass capillary and the air in the camera (P, interferences of porcelain powder).

equal intensity of incident radiation and equal amount of radiated substance (A justification of this procedure will not be set forth here[3]). The result is shown in Fig. 11 where the two curves, now rendered mutually comparable, are reproduced. It is seen that the amorphous cellulose gives rise to a broad diffuse band, having its maximum between the interferences A_0 and A_3A_4. On recrystallization this band disappears or is considerably reduced in intensity.

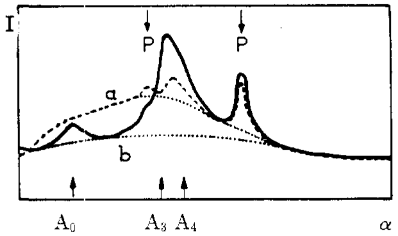

Fig. 11.—Intensity distribution of diffracted radiation of dry cellulose powder (a) before and (b) after recrystallization, reduced to equal intensity of incident radiation.

3. Integral Heats of Wetting.—It seemed of interest to determine the heat evolved on wetting the cellulose powder with a great excess of water before and after recrystallization, and to compare these figures with the integral heat of wetting of the original fiber material.

A small Dewar vessel closed by a thick piece of cork was used as a calorimeter. The temperature was read on a Beckmann thermometer and the very dry samples were brought into contact with the water in the calorimeter by crushing a thin-walled vessel, in which they were sealed, inside the calorimeter. The usual precautions were taken and the usual corrections made. The estimated experimental error amounted to plus or minus 3 per cent. All samples were dried at 110° in a current of dry nitrogen. The recrystallized powder was prepared by thoroughly mixing the powder with water in a small crucible to form a thick paste. Then the covered crucible was placed on a boiling water-bath until most of the water was evaporated. The remaining dry, recrystallized powder was then rigorously dried in the way indicated before. In each powder sample the percentage of porcelain grindings present was determined by ignition. The heat of wetting of pure porcelain powder obtained in a blank run of the mill was separately determined to be 2.3 cal./g. Corrections for the heat of wetting of the porcelain powder were calculated.

The outcome of the measurements is given in Table I. The rayon fibers were ground for one and one-half hours, the wood pulp fibers for five hours, this being the lapse of time after which microscopic examination showed that practically all fibers and fiber fragments of the original habitus had disappeared. The wood pulp fibers were prepared from a sheet by suspension in water followed by filtration on a Buchner funnel to form a cake. The latter was then carefully fluffed before the final drying to the very dry condition.

TABLE I

EFFECT OF GRINDING AND RECRYSTALLIZATION ON THE INTEGRAL HEATS OF WETTING OF RAYON AND WOOD PULP FIBERS

	Percentage of porcelain powder	Heat of wetting in cal./g. Found	Cor. for ash	Mean
		Viscose rayon		
Original fiber	..	22.4	..	21.7
	..	21.1	..	
Ground 1$^{1}/_{2}$ hour	10.7	27.5	30.5	30.0
	10.7	26.6	29.5	
After recrystn.	10.7	18.1	20.0	20.0
	10.7	18.1	20.0	
		Wood pulp		
Original fiber	..	14.9	..	14.3
	..	13.8	..	
Ground 5 hours	2.9[a]	28.6	29.4	29.0
	2.9	27.9	28.7	
After recrystn.	2.9	18.3	18.8	18.8
	2.9	18.3	18.8	

[a] The ash content of the wood pulp samples was smaller because balls of a harder material were employed.

4. Sorptive Capacity.—The sorptive capacity was examined by exposing the samples previously dried two hours at 110° to a current of conditioned air in the manner described in an earlier publication.[4] The dry weight and the ash content were determined afterward by drying at 110° in a stream of dried nitrogen and by ignition, respectively. The sorptive capacity of pure porcelain powder was separately determined and the figures for the cellulose samples corrected for the absorption due to the porcelain powder. (The difference between the dry weight of the porcelain powder at 110° in dry nitrogen and that after heating at the same temperature at which the ignition of the cellulose was carried out amounted to only 4% and was also accounted for.)

The results of the sorption experiments are recorded in Fig. 12. From these data the sorption ratios (ratio of the sorptive capacity to that of

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(3) See, *e. g.*, J. M. Goppel, Thesis, Delft, 1946.

(4) P. H. Hermans, "Contribution to the Physics of Cellulose Fibers," Elsevier, Amsterdam or New York 1946.

native cotton at the same relative humidity) were calculated and the average values taken. The latter are compiled in Table II together with the average values of the integral heats of sorption taken from Table I. In the last column the ratio of the two figures is given.

TABLE II

AVERAGE SORPTION RATIOS AND INTEGRAL HEATS OF WETTING

	Sorption ratio	Integral heat cal./g.	Ratio
	Viscose rayon		
Original sample	1.88	21.7	11.5
Ground $1^1/_2$ hour	1.98	30.0	15.2
Recrystallized	1.70	20.0	11.7
	Wood pulp		
Original sample	1.25	14.3	11.4
Ground 5 hours	2.12	29.0	13.7
Recrystallized	1.65	18.8	11.5
Native cotton	1	10.4	10.4

Discussion

In previous work[4] evidence has been brought forward that the density and the sorptive power of cellulose preparations depend on the percentage of crystalline substance and that the former two quantities approximately represent a measure for the latter. The percentage of the crystalline portion in native cotton, wood pulp and rayon fibers was estimated to be about 60, 50 and 25%.

The integral heats of wetting also run parallel with the percentage of amorphous substance, though there is no strict proportionality, since, for instance, the absorption ratio of rayon is about 1.9, whereas the ratio between the integral heats of wetting of rayon and cotton is 2.1–2.2.

The results obtained in the present investigation are in qualitative conformity with these earlier conclusions. The X-ray data show that the ground powders practically entirely consist of amorphous cellulose. These powders also show the highest sorption ratios and the highest heats of wetting (Table II). The difference with the original fibers is much greater in wood pulp than in rayon, in conformity with the higher percentage of crystalline substance in the former.

The difference between the sorptive capacity and the heat of wetting of the original samples and that of the ground powder is much greater in wood pulp than in rayon, in conformity with the fact that the former originally contains the greatest percentage of crystalline substance. Upon recrystallization in hot water, both wood pulp and rayon powder yield a product of approximately equal sorptive capacity and heat of wetting, these quantities, however, being markedly lower than in rayon. It would therefore seem that the percentage of crystalline substance reached on recrystallization of the amorphous products is somewhat higher than the approximately constant amount present in all kinds of rayon hitherto investigated.

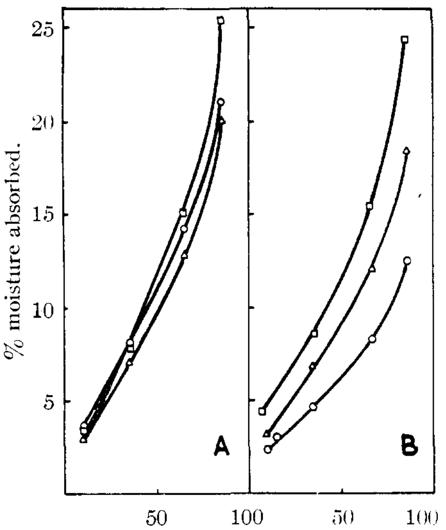

Fig. 12.—Sorption isotherms at 20° referring to rayon (A) and wood pulp (B): O, original sample; □, ground sample; △, ground sample after recrystallization.

It is not clear why the ratios between the heat of wetting and the sorption ratio of the amorphous powder (Table II last column) differ somewhat in wood pulp and rayon.

For reasons outlined in previous work,[4] quantitative deductions from this kind of result can only have an approximate character. Moreover, it is not certain that the ground products were quite free from small quantities of the original fibers, and more work with products ground for various times would be necessary to reach more precise conclusions. If, however, we venture to take the average figure of 1.68 as the sorption ratio of the recrystallized products and consider this figure as a measure of the percentage of amorphous substance contained therein, and if we further assume that native cotton contains 40% of amorphous substance,[4] the percentage of amorphous substance in the recrystallized powders would be 1.68 × 40 = 67%. By the same reasoning rayon would contain 1.88 × 40 = 75% amorphous substance.

The difference between the heat of wetting of the amorphous and that of the recrystallized products amounts to 10 cal./g. or 1.62 kcal./mole in both cases investigated. Since recrystallization also occurs on wetting the powder with water at room temperature (though the diffraction pattern so obtained is somewhat blurred) we may tentatively assume that the fraction of crystalline substance, x, which is formed when the amorphous powder is wetted with water in the calorimeter, is equal to that present in the recrystallized powder. The heat of wetting of the amorphous powder may then be represented by

$$(1 - x)W_{\text{am}} + xH_{\text{cr}} + xH_{\text{hydr}}$$

and that of the recrystallized product by

$$(1 - x)W_{\text{am}} + xH_{\text{hydr}}$$

where W_{am} is the heat of wetting of amorphous cellulose, H_{cr} the heat of crystallization of cellulose II and H_{hydr} the heat of hydration of cellulose II (which forms a crystalline hydrate).[4] The difference of 1.62 kcal./mole is, hence, xH_{cr}. Now, the heat of crystallization of β-glucose is about 5.5 kcal./mole and that of cellulose will be also very near this value. This leads to the expression $5.5x = 1.62$ or $x = 0.28$, which corresponds to 72% amorphous substance, a figure of the same order of magnitude as that previously derived from sorption data.

From the X-ray data shown in Fig. 11 we may also venture to compute this figure. To that end we may assume that the intensity of the diffracted radiation in the maximum of the broad "amorphous" band represents a measure for the percentage of amorphous substance. We then find (in arbitrary units; height in mm. of the photometer curves) 26 in the ground powder from ramie and 16 in the recrystallized one. Taking the former as being 100% amorphous, the percentage of amorphous substance in the latter would be $(16:26) \times 100 = 62\%$. This figure is in approximate agreement with the figure of 67% as derived from sorption data.

If we take the surface of the whole area under the dotted curves in Fig. 11 instead of their maximum height as a measure of the amorphous percentage, we find 72% instead of 62%. However, for several reasons (not to be outlined here) the former procedure seems preferable.

There is, however, another, perhaps more important conclusion which may be tentatively derived from this investigation, namely, that the intensity of the "background," measured under the crystalline interference A_3 of cellulose II, if corrected for scattering by air and for absolute intensity of the incident beam, may be taken as a measure of the percentage of amorphous substance. This means that this quantity must be approximately equal in all regenerated cellulose fibers provided our former deductions[4] are correct. This subject will be dealt with in another paper.

Finally it should be mentioned that K. Lauer, *et al.*,[5] in earlier reports on the heats of wetting of ground and recrystallized grinding products of cellulose fibers have stated that there was no difference whatever with those of the original samples. This statement is incorrect, just as many other items in that publication, which also omits most of the essential experimental details of the work.

Acknowledgment.—We are indebted to Dr. J. J. Hermans of this Laboratory for coöperation in the experimental work and for discussion of the subject matter. The electron micrographs were taken by the "Institute for Electron Microscopy" with an instrument constructed in the Laboratory of Technical Physics of the Technical College in Delft, Netherland. The X-ray work was carried out by one of us (W.) as a guest in the same laboratory.

Summary

In conformity with a paper by Hess and coworkers cellulose fibers can be transformed into approximately wholly amorphous products by grinding in a vibrating ball mill and these products partly recrystallize on heating with water. A quantitative study of the intensity distribution in X-ray photographs of the amorphous and recrystallized powders from ramie fibers shows that the amorphous substance gives rise to a broad band whose maximum intensity lies at the site of the A_3 interference of cellulose II (hydrate cellulose). Computation of the intensities leads to the conclusion that the recrystallized products contain about 60–70% amorphous substance.

The integral heats of wetting and the sorptive capacities of the grinding products of rayon and wood pulp were determined before and after recrystallization. The results obtained are in fair conformity with the foregoing and with previous deductions on the percentage of crystalline substance in various cellulose fibers.

UTRECHT, THE NETHERLANDS RECEIVED JULY 2, 1946

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[5] K. Lauer, R. Döderlein, C. Jäckel and O. Wilde, *J. makrom. Chem.*, **1**, 76 (1943).