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## TRANSVERSE SHRINKAGE OF INDIVIDUAL FIBRES BY MICRO-RADIOGRAPHY

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**Synopsis**—Micro-radiography has been used to determine the width and moisture content of individual pulp fibres during their drying from the swollen state. The method, which employs soft X-rays to produce contact radiographs of the fibres, is described and results are given for a spruce sulphite wood pulp. An assessment of changes in the thickness of the fibres while drying is also given.

#### Introduction

ALTHOUGH various mechanisms have been suggested to explain the shrinkage of paper, it is reasonably certain that the largest proportion of the shrinkage originates from the transverse shrinkage of the constituent fibres. In a theory of shrinkage presented by two of the authors at the last symposium.<sup>(1)</sup> the potential transverse shrinkage of the fibres was quoted as one of the factors important in deciding the ultimate structure and properties of the sheet. Paper can, in the extreme, display as much as 20 per cent shrinkage and, to justify attributing a substantial part of this to the fibres, it follows that their transverse shrinkage must be of the same order as this figure. A value of the order of 10 per cent has been deduced<sup>(2)</sup> from values of the saturation moisture content of fibres by calculating the equivalent volume. hence linear, dimensional changes when drying to equilibrium with 65 per cent rh. No attempt appears to have been made to measure the transverse shrinkage of fibres when freely drying before the work carried out in the authors' laboratories and reported elsewhere.<sup>(4)</sup> This work proved that fibres shrink in width by the very large amounts necessary to be substantially responsible for paper shrinkage.

The values of transverse fibre shrinkage reported were obtained by direct

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measurement of width changes when fibres were dried to equilibrium with 20 per cent rh from the state of being completely immersed in water. Even within one fibre type and treatment, these results showed quite a large spread about the mean, far greater than could be attributed to experimental errors. Unfortunately, the method used gave no measure of the loss of moisture associated with the observed dimensional changes, nor was it capable of revealing any intermediate relationship between dimension and moisture content during the drying process.

Variation in the rate of paper shrinkage during water removal has been reported in the literature.<sup>(2,3)</sup> The results in Fig. 1 were obtained from the papermachine and the author suggested that the shrinkage behaviour could be represented by three straight lines as shown. We have carried out a similar investigation into the behaviour of handsheets while freely drying and the results are shown in Fig. 2. In this, although three straight lines could be



Fig. 1—Relationship between water content and shrinkage of wet web—Rance<sup>(2)</sup>

drawn through the points, especially in the case of the higher beaten pulp, there is no justification for supposing that the curve should not be a smooth one as drawn. What is confirmed, however, is that the shrinkage rate with respect to the moisture ratio is very low at the wet end of the range, then increases and becomes very high during the removal of the last 20–30 per cent of the water.

In order to fill in some of the gaps in the knowledge of fibre shrinkage

#### Fibre transverse shrinkage

that remained after the determinations referred to  $above^{(4)}$  and with the ultimate aim of relating paper shrinkage more closely to the behaviour of fibres, it was considered essential to study fibre shrinkage in more detail and, in particular, to determine the exact relationship between the transverse dimensional change of fibres and their moisture content during the drying phase.







The method chosen for this study and described in this paper was that of contact micro-radiography, in which the specimen is placed in close proximity to a photographic plate or film and illuminated by a point source of X-rays that impinge normally on the film. For monochromatic X-rays, the absorption follows the well-known Lambert's law—

$$I_T = I_0 \exp(-\mu t)$$

where  $I_T$  and  $I_0$  are respectively the transmitted and incident intensities,  $\mu$  is the linear absorption coefficient and t is the thickness of the specimen in the direction of the X-ray beam. The linear absorption coefficient varies rapidly with the wavelength of the X-rays and with the elemental composition of the absorbing material. For cellulose materials, the absorption



Fig. 5—Diagram of the X-ray camera

coefficient is large enough in the region of a few Ångstroms wavelength for appreciable absorption to occur while passing through specimens of the order of thickness of a fibre. Thus, it is possible by enlargement of the film in the light microscope to obtain the transverse dimensions of the fibre by direct measurement and, from the contrast of the image, it is possible also to determine the change in total mass—hence, moisture content—of the fibre.

## Apparatus

THE source of the X-rays was a Philips CMR5 X-ray equipment (Fig. 3). The accelerating voltage applied to the X-ray tube could be varied from 1.5 kV to 5 kV, but at any one voltage the emergent radiation was not monochromatic, but had a spectrum of the type shown in Fig. 4.



Fig. 3—The X-ray equipment (centre foreground) and subsidiary apparatus: the special camera is fixed to the protruding arm that houses the X-ray tube



Fig. 6—The camera dismantled, showing the specimen support and the film carrier

Previously, contact micro-radiography has usually involved close proximity between the specimen and emulsion and, in some cases, specimens have even been dried on to the emulsion to ensure intimate contact. For our work, it was essential that the wet fibres were spaced away from the emulsion to allow complete freedom while drying. On the other hand, owing to the finite size (0.3 mm square) of the X-ray source, the ratio of the distances from source to specimen and from specimen to emulsion had to be sufficiently large to ensure that the penumbral region did not impair the resolution. For the purposes of this experiment, a special camera attachment was therefore made to be positioned against the X-ray tube instead of the camera provided. This camera (shown diagramatically in Fig. 5) consisted of three basic units—an upper and a lower brass tube, between which was sandwiched a brass plate, sealed together by rubber O-rings. The fibre specimens were



Fig. 7—Diagram of the glass system for evacuating the camera

supported on a perforated metal foil (1.6 mm diameter perforations), which in turn was fixed across the bottom of a hole in the brass plate. The X-ray film was held in a carrier so that the emulsion was immediately below the specimen support. The specimen to emulsion distance was 0.25 mm and the source to specimen distance 16.5 cm. The film carrier could be rotated by means of a shaft passing through a vacuum seal, thus allowing eight exposures to be made by successively positioning different sectors of the film under the specimen without disturbing the camera or specimen. The construction of the camera was facilitated by the fact that the most even and intense part of the X-ray illumination occurred off-axis and so the specimen was placed to one side of the centre, as shown, to coincide with the optimum region. Fig. 6 is a photograph showing the specimen support and the film carrier.

Soft X-rays are strongly absorbed by air and to ensure that the X-ray intensity at the specimen was not greatly reduced, it was desirable or even essential to remove the air from the camera in which the exposures were carried out. Evacuation of the camera to remove the air was also the means of drying the wet fibre specimens in a controlled manner. A vacuum system, shown diagramatically in Fig. 7, was constructed to which the camera tube was connected by means of metal bellows.

## Experimental procedure

ABOUT 0.5 ml of a dilute fibre suspension was put on to the specimen support and another metal foil, identically perforated, was placed on the drop and pressed down until it was in contact with the lower support. Provided this was done carefully, the water flowed on to the top of the upper foil, leaving fibres spanning across the perforations and held between the two foils. The drop of water was retained, thus enabling the fibres to be put into the camera while still immersed and saturated.

Once the camera had been assembled, with the wet specimen in position, it was evacuated until the pressure in the camera was not quite as low as the saturated vapour pressure of the water (17.5 mm Hg at 20°C). This was found, by experience, to correspond to a pressure as read on the mercury manometer of about 15 mm, owing to the resistance while pumping in the connection to the camera. The camera was then isolated from the system, which was pumped rapidly to a pressure of 100 milli-torr.\* The T-stopcock was positioned so that the left limb of the oil manometer and the by-pass of the capillary were closed and the camera was reintroduced into the system and slow evacuation commenced via the capillary tube. It was found that a slight fluctuation of the pressure shown by the oil manometer indicated when the 'free' water menisci had just evaporated from the fibre suspension, then the camera was isolated and the first exposure made. The oil manometer was read to record the pressure, which was usually about 1.9 cm Hg during the first exposure. Although there was still some X-ray absorption by the water vapour in the camera, it was not sufficient seriously to prolong the exposures.

After the first exposure, the specimen was dried in successive stages by a similar procedure and radiographs obtained at various moisture contents. The final pressure in the camera was 200 milli-torr and the fibres were then assumed to be dry (this partial pressure of water vapour corresponds to a

<sup>\*</sup> Torr = mm mercury pressure at  $0^{\circ}C$ 

relative humidity of very roughly 1 per cent). An enlarged print of a typical X-ray film is shown in Fig. 8.

The X-ray tube was run at 4.9 kV, with an emission current of 2 mA for all exposures. The film used was Kodak experimental film, V6028 developed



Fig. 8—Enlargement of a typical X-ray film with eight exposures  $[\times 5]$ 



P = pulp fibre; T = Terylene fibres



for 5 min at  $68^{\circ}$ F in Kodak Universal developer. The exposure times were 12 min when the specimen was wet and 4 min when dry.

## Analysis of the micro-radiograph image

THE determination of the thickness (or mass) at any point of the specimen is carried out from the optical density of the image of the radiograph. It is impossible to do this by direct application of the law of X-ray absorption, as the incident intensity is not monochromatic, but has the spectrum shown in Fig. 4. Consequently, it has to be done by means of comparison objects of known thickness, composition and density, which are radiographed at the same time as the fibres and are sufficiently close to them to ensure that the incident intensity is essentially the same. It was also desirable that the comparison objects or calibration masses should not change during the drying process—in other words, their moisture uptake should be extremely small.

The calibration was achieved by depositing with the pulp fibres thin polyethylene terephthalate (Terylene) fibres of circular cross-section, initially



Fig. 10—Densitometer trace of the scan across the image of fibre No. 7 (shown in Fig. 9)

introduced into the dilute suspension of pulp fibres and dried down on to the specimen holder. The mass at any point of the specimen could then be determined by comparing the optical density of the specimen image at that point with the optical densities of the images of the Terylene fibres whose thickness and density were known.

Two diameters of Terylene fibres were always included—6.2 and 15.4  $\mu$  and sometimes fibres of 21.4  $\mu$  were also added. The pulp fibres that were analysed were always chosen so that there was at least one of each size of calibrating fibre in their near vicinity.

Optical densities of the images were compared by making an enlargement of the X-ray film on photographic plates in a light microscope at a magnification of 116 times. A print of such an enlargement is shown in Fig. 9.



Fig. 11—Densitometer traces across the three calibrating fibres (shown in Fig. 9): fibre diameters given in microns

The procedure for analysing the images on the photographic plate was as follows. The fibres were scanned across their widths by a double beam, scanning micro-densitometer using a slit size of  $2 \text{ mm} \times 0.1 \text{ mm}$  on the plate (2 mm dimension parallel to the fibre axis). The slit size relative to the fibres on the original X-ray image was thus  $17 \times 0.85 \mu$ . The position of scan was



Fig. 12-Calibration curve derived from traces of Fig. 11

located by means of fine scratches made on the edge of the plates (in this way almost exactly the same part could be scanned on the selected fibres throughout the series of eight plates representing conditions at the successive stages of drying). Both the pulp fibres and the calibrating Terylene fibres were so scanned on each plate. The traces corresponding to the scans indicated on Fig. 9 are shown in Fig. 10 and 11. From these scans, a plot of optical densities of the Terylene fibre images against their thicknesses was made as



Fig. 13

Fig. 14

shown in Fig. 12, which was then used to convert the optical densities of the trace of the pulp fibre into equivalent thickness of Terylene. The area under the corrected scan was determined by summation of the ordinates and this was used as a measure of the total mass, still in terms of Terylene, of a slice of the fibre of width corresponding to the height of the scanning spot.

Besides, from each scan, the *width* of the wood fibre was directly measurable and, from a knowledge of the total magnification, could be converted into real dimensions.

This analytical procedure was adopted for each plate corresponding to each successive stage in the drying of the specimen and the data was used to plot a graph of the width of the fibre against its equivalent total Terylene mass. Such graphs are shown in Fig. 13–15. (For simplicity, the mass was left in terms of arbitrary, but consistent units, representing the area under the corrected densitometer scans, as only ratios of mass are of ultimate interest.) A smooth curve having the best visual fit was drawn through the points. As can be seen from these graphs (Fig. 13–15), there was some scatter, which was mainly attributed to uncertainty in the values of mass. The width determinations were considered the more reliable, as they were obtained by



Fig. 15

direct, linear measurement and did not involve any indirect calibration and conversion process as did the mass or moisture content determinations. This is also borne out by the fact that, as drying proceeded, the width measurements always decreased in a sensible manner, whereas the values of mass were on occasions more erratic and sometimes showed an increase rather than a decrease. As the specimens studied had a range of widths and mass, in order to compare results, the last step in the analysis was to reduce the changes of the measured parameters to percentages referred to the final dry values. It was assumed that the final dry width was that actually measured from the last exposure, which was always taken with a final pressure in the camera lower than 200 milli-torr. The final mass of the fibre was taken as the mass corresponding to the final width and read from the drawn curve. This dry value represents the fibre substance, mainly cellulose. Values of widths when wet



Fig. 16

Fig. 18

were taken from the drawn curve and expressed as a percentage of the reference dry value. Corresponding values of wet mass were taken at the same time and the difference between these and the reference dry value represented moisture. After correcting for the difference in the mass absorption coefficients of cellulose and water, the equivalent Terylene masses could then be converted to percentage moisture contents of the fibre. For each fibre, a graph of percentage change in width against percentage moisture content was plotted (Fig. 16).

#### Fibre transverse shrinkage

#### Results

THE graphs of fibre width against equivalent Terylene mass are shown in Fig. 13–15 for seven specimens, all of unbeaten, spruce sulphite pulp. Specimens No. 6, 7 and 9 were never-dried fibres, whereas the others were



Fig. 17—Enlarged images of specimens studied [total magnification  $\times$  350]

from a redisintegrated dry pulp lap. In the case of fibres numbered 1, 4, 5 and 6, adjacent scans were carried out and are denoted by the suffixes a, b, c, etc. A print of the fibres analysed is given in Fig. 17, except for No. 7, which has 10-c.p.w. I

already been illustrated in Fig. 9. The existence of scatter of the points has been remarked upon and, for two fibres (No. 3 and 8), the scatter was so pronounced that it was very difficult to fit a curve to the points. These two specimens have been omitted from the results.

The derived graphs of percentage width change against percentage loss of moisture content (by weight) are given in Fig. 16. With the exception of

Specimen no.	Dry width, microns	Mean dry thickness, microns*	Total moisture loss, per cent	Total width change, per cent	Total mean thickness change, per cent*
1a 1b 2 4a 4c 4d 4c 4f 5a 5b 5c	40 39 38 40 40 38 38 38 38 37 59 59 59 59	4.7 4.7 5.0 2.5 2.5 2.6 2.6 2.6 2.8 2.8 2.2 2.4 2.3	54 52 53 44 41 47 58 47 44 36 31 30	22 23 20 17 17 21 21 20 21 8 8 8 8	50 47 50 44 40 43 56 44 39 45 37 35
6a 6b 6d 7 9	19 19 19 35 37	6.1 6.0 6.7 3.7 3.6	60 54 59 38 58	34 33 34 24 19	44 37 43 28 59

TABLE 1-FIBRE DIMENSIONS AND CHANGES (BASED ON DRY VALUES)

\* Based on a value of the dry wall density of 1.54 g/cm<sup>3</sup>

fibre No. 6, the rate of shrinkage with respect to loss of moisture increases as the fibre gets drier. The total width shrinkages range from 8 per cent for fibre No. 5 to 34 per cent for fibre No. 6. The total moisture losses range from 30 per cent (No. 5) to 60 per cent (No. 6). Shrinkage and moisture loss values for all fibre specimens are given in Table 1. These total values, from wet to dry, do not necessarily represent the changes occurring when drying from saturation, as the first and wettest values were obtained when it was judged that the free water menisci had just evaporated. It may have been the case that a part of the water of swelling had already been removed before the first exposure was made.

By making the assumptions that swelling is a simple bulk effect, the density of dry fibre wall is  $1.54 \text{ g/cm}^{3(5)}$  and the fibres approximate to a rectangular cross-section, it is possible to calculate mean percentage *thickness* changes against percentage moisture losses for the fibres. This has been done



Fig. 19—Representations of fibre cross-sections in terms of Terylene: black areas represent the fibre in the saturated state and hatched areas the fibre in the dry state

and the results are shown in Fig. 18. With the exception of specimen No. 6, the graphs are nearly linear and the values of total thickness shrinkages are seen to be greater than the corresponding values of width shrinkage. In other words, indications are that, when the fibres lost moisture, they contracted more in their thickness than in their width (bearing in mind that, when fibres dry and collapse or when they are deposited from suspension, they tend to lie with their largest cross-sectional dimension in the horizontal plane).

A representation of the changes in cross-section of some of the fibres is shown by the silhouettes in Fig. 19. These show, *in terms of Terylene*, the profile of the fibre drawn symmetrically about a central, horizontal axis and derived from the actual heights of the densitometer scans across the fibres. (These scans give only the total thickness at a point and not the precise cross-sectional shape.) The thicknesses are left in terms of Terylene, as there is no way of deciding which points across the width of the fibre correspond to each other when wet and dry, as the fibre in the dry case has contracted in width with a relative movement of the corresponding points.

### Accuracy

ULTIMATELY, two parameters were determined from each micro-radiograph —the width of the fibre and the moisture content of the slice of fibre whose width was measured.

Errors in the width measurement could have arisen from two sources—the resolution of the edges of the fibres and the fact that the fibre was scanned with a rectangular spot of finite width. Resolution was limited by the grain of the film to something of the order of half a micron. It was limited also by the penumbral region (owing to the finite source size) again to about half a micron, but deeper consideration of these two factors indicates that the errors they produce in the calculation of percentage width changes through a series of micrographs are almost negligible. The effect of finite slit width is that the recorded trace representing the density of the image starts smoothly, not abruptly, as the advancing edge of the slit meets the fibre image. In practice, other effects, referred to below, were more significant in confusing the commencement of the fibre scan and making it difficult to locate precisely.

Errors in the determination of moisture content can be attributed to two factors—the accuracy of mass calibration by means of the Terylene fibres and the accuracy of scanning and mass determination of the pulp fibre itself.

Errors in calibration could have arisen from inaccuracy of the value of the thickness of the Terylene fibres where actually scanned, but these fibres appeared from their micrographs to be of fairly constant width and thickness. The micrographs and cross-sections of the fibres indicated that they were circular. The diameters of the fibres were measured by an image splitting eyepiece to an estimated accuracy of  $\pm 0.25 \ \mu$ . Sideways vibration of the fibres was sometimes suspected, which would have the result of slightly lowering their effective thicknesses. Granularity of the X-ray emulsion impaired the shape of single scans and for this reason five adjacent scans of the Terylene fibres were made and averaged. These errors were not great, were of a random nature and were minimised by the process of plotting curves through the set of points for each specimen.

For the purposes of calculating the mass absorption coefficient of dry fibre material, the assumption was made that it consisted solely of cellulose taking for its formula  $(C_6H_{10}O_5)_n$ . This does not give rise to any serious error, as the absorption coefficients of other materials likely to have been present are not very different from that of cellulose.

Possibly the most serious source of error arising from calibration is the fact that the diameter of the thinnest calibrating fibre was as large as  $6.2 \mu$  (equivalent to  $4.9 \mu$  cellulose). The calibration curves, moreover, were drawn through only four points. Great confidence could not be placed in the precise position or shape of the line drawn on the calibration curve in the region of a few microns. This factor will be studied further and it is hoped to develop an improved method of calibration to check these results.

Errors in scanning and mass determination of the pulp fibre could have arisen from granularity of the X-ray film, both in the fibre image and in the background of the scan. The effect on the background or base-line can be seen from Fig. 10. The best value for the background had to be selected by eye. The effect of granularity on scan within the fibre cannot be assessed, as there was no means of distinguishing between fibre features and grain.

At an early stage in the experiments, before the experimental techniques had been finally established, the accuracy of the mass determinations was estimated by making eight exposures of the same specimen, actually giving different lengths of exposure to the X-rays. The total spread from maximum to minimum mass values was  $\pm 10$  per cent of the mean value. The magnitude of the random errors can be assessed from the scatter of the points in the plots of Fig. 13–15. The degree of scatter varied from one specimen to the next, which is regarded to be due to variations in granularity of the X-ray film. The effect of the random errors was minimised by the drawing of smooth curves through the points of these graphs.

As it is intended to obtain more results before presentation to the symposium, a final estimate of accuracy will be postponed until the results are complete.

## ADDENDUM

#### Additional results

FURTHER results have been obtained for eleven specimens of unbeaten spruce sulphite fibres (numbered 10 to 20) and 13 specimens beaten for 60 min in a Valley beater to a freeness of 85 s.R. (numbered 21 to 33). (Unbeaten specimens 1–5 and 10–16 occurred on the same radiograph; specimens 6–9 on another and 17–20 on a third. Beaten specimens were on two radiographs, grouped 21–24 and 26–33.)



The graphs of fibre width against equivalent Terylene mass are shown in Fig. 20–23 with the exceptions of specimen 25, which has been omitted owing to excessive scatter and of specimen 26, which could not be conveniently included on these composite graphs because of its very large width.

With specimens 17–20 (unbeaten fibres)—radiographed at the same time a deliberate attempt was made to ensure that the fibres were still saturated at the time of the initial measurement by making the first exposure at an earlier stage in the pumping procedure than for the other specimens. There was some



Fig. 24—Unbeaten fibres

Fig. 25—Beaten fibres (60 min Valley)

evidence in this initial exposure that free water menisci still existed between some fibres.

The derived graphs of percentage width change against percentage loss of moisture are given in Fig. 24 and 25. A print of some of the beaten fibres analysed is given in Fig. 26.



26 (3 per cent)

29 (29 per cent)



31 (45 per cent)

32 (41 per cent)

Fig. 26—Enlarged images of some of the beaten fibres studied (total magnification  $\times$  350): the total width shrinkage of each fibre is given as a percentage of the dry width

#### Fibre transverse shrinkage

Summaries of the total shrinkage and moisture losses of these specimens are given in Table 2. The thickness changes have been calculated as before and the graphs of percentage thickness changes against percentage moisture losses are shown in Fig. 27 and 28.

Specimen No.	Dry width, microns	Mean dry thickness, microns*	Total moisture loss, per cent	Total width change, per cent	Total mean thickness change, per cent*
Unbeaten fibre 10 11 12 13 14 15 16 17 18 19 20	24 23 41 34 46 27 21 49 44 34 28	5.7 3.5 1.6 1.8 1.5 1.6 4.4 2.6 2.8 3.1 7.9	45 46 55 44 35 36 39 111 79 121 56	29 22 11 14 11 20 30 18 11 17 19	32 41 66 47 38 31 24 130 101 145 57
Beaten fibre 21 22 23 24 25 26 27 28 29 30 31 32 33	30 37 35 31 26 59 30 26 23 33 28 22 30	$2.2 \\ 1.4 \\ 2.7 \\ 5.1 \\ 1.3 \\ 2.2 \\ 2.5 \\ 5.2 \\ 2.8 \\ 1.2 \\ 3.9 \\ 2.9 \\ 1.2 $	78 77 69 52 54 87 78 101 98 127 74 80	40 13 38 24 25 3 34 31 29 29 45 41 25	57 94 50 45 77 74 68 98 95 105 52 79

TABLE 2-FIBRE DIMENSIONS AND CHANGES (BASED ON DRY VALUES)

\* Based on a value of the dry wall density of 1.54 g/cm<sup>3</sup>

### Effect of rate of drying upon shrinkage

As THERE was no precise control over the rate at which the fibres were dried, it was considered desirable to check whether the rate of drying, within the limits set by the apparatus, influenced the magnitude of the shrinkage.

To do this, one batch of unbeaten fibres was dried at a very slow speed of pumping and another batch at the highest attainable pumping speed. The shrinkages of the fibres in each batch were compared and found not to be significantly different. Thus, as no difference was found between the two extremes of pumping, it was assumed that any variation of drying rate that may have occurred during the principal experiment did not have any effect on the measured values of shrinkage.

#### Effect of fibre width upon shrinkage

FROM an examination of the results given in Tables 1 and 2, there is some suggestion that an inverse correlation exists between total fibre shrinkage and dry fibre width. The existence of such a relationship was tested by a regression analysis of shrinkage against fibre width on the results obtained for the preceding investigation.





Fig. 28-Beaten fibres (60 min Valley)

The correlation coefficient obtained from this regression was -0.686, which is significant at the 1 in 1 000 level. (The correlation coefficients for the two groups taken separately for the extreme drying rates were -0.703 for rapid and -0.667 for slow drying—not significantly different.) The value of the coefficient implies that roughly half of the variation in total shrinkage can be accounted for by the variation in fibre width.

#### Fibre transverse shrinkage

## Further discussion of accuracy

IN THE original discussion of accuracy, the uncertainty of the shape of the calibration curve in the region of interpolation between points determined by zero mass and the thinnest available Terylene fibres (6.2  $\mu$ ) was considered as a possible source of error, particularly as the thickness of the majority of cellulose fibres falls within this range.

Doubts in this respect have been eliminated by radiographing a Terylene wedge having a linearly increasing thickness from 0 to 20  $\mu$  obtained by obliquely sectioning a piece of sheet material. The wedge linearity was confirmed by light interferometry. The continuous traces of optical density against Terylene thickness derived from this wedge were of exactly the same shape as the curve drawn through the measured points of Fig. 12.

	1	
	Unbeaten	60 min Valley beaten
Wet width, $\mu$	43	41
Dry width, $\mu$	36	32
Average total width shrinkage, per cent	18	29
Wet thickness, $\mu^*$	5.4	4.8
Dry thickness, $\mu^*$	3.4	2.8
Average total thickness shrinkage, per cent*	60	75
Average total moisture loss, per cent	57	81

TABLE	3
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\* Based on a value of 1.54 g/cm<sup>3</sup> of the dry wall density

For reasons previously given, the scatter in the plots of Fig. 13–15 and Fig. 20–23 has been assumed to be mainly due to random error in the determinations of the mass values. The standard deviation of the spread of the values of mass about the curves drawn through the points has been determined and expressed as a percentage of the mean mass value. This was found to be 5 per cent for the unbeaten fibres and 7 per cent for the beaten fibres.

## Summary and conclusion

THE RESULTS for 15 unbeaten and 12 beaten fibres from a dried spruce sulphite pulp are shown in Fig. 16, 24 and 25 in the form of width change against moisture content change (three never-dried fibres are also shown in Fig. 16). The changes in width and moisture are expressed in terms of the final dry values. Total changes of dimensions and moisture content for all the fibres are given in Tables 1 and 2. Average values taken from these tables of the figures for total width and thickness shrinkages and moisture content change for beaten and unbeaten fibres are given in Table 3. The mean initial wet widths and thicknesses are also included.

The basic objective of the work that has been described in this paper was the determination of the relationship between the transverse shrinkage of papermaking fibres and their moisture content throughout their drying phase. It will be of ultimate interest to study the variation of this shrinkage behaviour between types of fibre and methods of fibre treatment, but so far the study has been limited to the investigation of the difference between two levels of beating for one pulp, originally in dry lap form.

It is intended to obtain more results by means of this technique, from which it will be possible to draw more confident conclusions and so arrive at a better understanding of the shrinkage behaviour of fibres.

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# Discussion

**Prof. H. W. Giertz**—It must be questioned whether it is possible to draw any conclusions about the fibre's geometrical structure from absorption measurements. In the present case, the assumption is made that the fibre material consists only of fibrillar cellulose, which cannot be penetrated by nitrogen and that the microfibrils form concentric lamellae separated from each other by air. It is further assumed that all nitrogen is adsorbed on such lamella surfaces. Let us also assume that the fibre contains hemicellulose (which could be located between the lamellae) and that the hemicellulose, if dried in a proper way, because of its amorphous nature, forms an open structure that can be penetrated by the nitrogen. If this is the case—and I cannot see why it should not be—I would expect the absorption, if calculated per gram of substance, to be very high in the hemicellulose within the material instead of on external surfaces.

It is obviously without sense to calculate a 'surface' from such measurements and it is, so far as I can see, impossible to use experimental data of this kind to draw conclusions about the internal structure of the material when the proportion of cellulose to hemicellulose and the specific absorption of hemicellulose are unknown. Have you made corresponding measurements on typical amorphous materials such as hemicellulose and lignin?

Dr J. E. Stone—Let me say first of all that surfaces measured by nitrogen adsorption are real and the values of area calculated accurate—in many cases, these have been checked by independent measurement. Secondly, simple geometry can show that surface areas of the order  $100 \text{ m}^2/\text{g}$ , as in our swollen pulp samples, correspond to particles of the order of 100 Å.

Following this line of reasoning, all we have done in producing the multilamella model is to postulate a shape for the basic particle in the swollen cell wall—the reason for the choice of the lamella rather than some other shape being discussed in our previous publication.<sup>(4)</sup> Of course, the thickness we have given in this paper for the lamellae are average ones and it is extremely likely that there is a distribution of sizes about these averages, but it is doubtful whether the distribution could contain many particles of molecular dimensions, since the specific surface area of these would be well over 1 000 m<sup>2</sup>/g.

## Fibre shrinkage and pore structure

Finally, it should be noted that there is a distinct difference between the adsorption of the non-polar nitrogen molecule and the polar water molecule. Early attempts to measure the surface area of cellulose from water isotherms have been shown to be quite invalid, as the water molecules not only collect on the surfaces, but enter between the cellulose molecules (at least in the disordered regions)—into what we have termed microreticular pores. Much confusion can result from regarding the adsorption of the two vapours as the same.

**Dr B. Leopold**—In your paper, you discuss the problems connected with measuring the density of the dry cell wall and compared your results with those obtained using microscopic methods, then you promise to settle the question of the discrepancies found. Have you done so?

**Dr Stone**—A discussion of cell wall density and its measurement (mainly by the mercury intrusion method) is the subject of a paper I have submitted for publication. It can be summarised by saying that nitrogen adsorption, mercury intrusion and low angle X-ray scattering all show the cell wall of native cellulose fibres to be essentially non-porous. The only data that indicate a porous wall have been obtained by microscopic measurement of cell wall cross-sectional area and suggest that the method should be examined critically by its practitioners.

**Dr O. J. Kallmes**—The picture that you presented of the structure of fibres was presented also by Kerr and Bailey in the thirties. They showed that the cellulose and lignin in wood are arranged in coaxial layers and the density of both of them varies from layer to layer; thus, you expect to get the kind of structure in delignified fibres that you obtained here. They also show that a large proportion of the fibres have a radial, coaxial orientation—that is, the layers in the original wood tend to radiate out in the wall like the spokes of a wheel. Have you ever found such structure in the sections? It seems that a structure such as you propose would fibrillate easily during beating, whereas that with the radial orientation would be more difficult to fibrillate. This is the practical significance of my point.

**Dr** Stone—We have taken many cross-sections of fibres and no two are alike. This makes it very difficult to say just what the structure is and it may be wrong to make generalisations, but a structure based on lamellae coaxial with the cell axis is consistent with the Frey-Wyssling model for microfibrils, on the observation of sheet-like material peeling from beaten fibres, on the swelling behaviour of fibres and on many light and electron micrographs of fibre crosssections that have appeared in the literature. This is reviewed in reference 4 of the paper.

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Mr P. A. Tydeman—The lamellar concept of fibre collapse explains not only the anisotropy of fibre shrinkage, but also the inverse relationship between transverse shrinkage and fibre width. When seen in plan view, a thinwalled, collapsed fibre has a smaller proportional component of radial shrinkage due to lamellar collapse than has a thick-walled and cylindrical fibre.

Mr L. G. Samuelsson—In your curves of change in fibre widths against moisture loss, there is a slope at moisture contents as high as 120 per cent. When do these curves level out completely—that is to say, at what moisture content does drying start to affect the fibre wall? My second question is at what moisture content does the lumen water disappear during drying of a sheet of paper?

*Mr Tydeman*—The case of fibres exhibiting large moisture loss (perhaps, even up to 120 per cent) brings us back to a consideration of what is free water and what is bound water. From the radiograph of these fibres, they are obviously very wet and, in fact, have the appearance of a perfect cylinder of material very deficient in the fibre structure seen when dry. This may indicate that, starting our measurements at such a wet stage, the radiographs show water on the fibre surface and (as the shrinkage curves demonstrate) loss of this water results in very little shrinkage. Perhaps by taking the moisture loss that does produce shrinkage, we can term this *water of shrinkage*. To me, this work fails to give a mean moisture content at which the lumen collapses: Robertson's work is more likely to do so.

Dr A. A. Robertson—I am not sure that I can answer the question of when the water from the lumen begins to disappear. When one considers the volume of the fibre in the tree and makes the assumption that pulping occurs without fibre shrinkage, it may be supposed that a fibre can hold as much as 300 per cent water by simple volume considerations. Hydrodynamic specific volumes are in agreement with this sort of figure. One is then led to conclude that, when water is removed below this amount, the fibre will begin to collapse. Since the lumen is the largest void, it can be expected to empty first. I suggest therefore that a quick answer to the question is 300 per cent moisture.

**Mr P. E. Wrist**—From the course of the discussions today and from several of the symposium papers, I believe a new viewpoint is emerging of the paper web and of the relationships between the water and the cellulose it contains, particularly during the drying cycle.

The old view has regarded the web as a network of fibres in which the fibres are the unit elements of the structure and voids between them contain the bulk of the water to be removed during pressing and drying. The major portion of the drying cycle was considered to be concerned with the removal of

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this extra-fibre water and perhaps only in the final stages of drying were we concerned with the removal of the 'water of swelling' contained within the fibres themselves. This water was regarded as being bound to varying extents within the fibres and to be different in its properties and behaviour forces the water external to the fibre. By contrast, the unit of the network now appears to be at least the fibre lamella, probably the fibril itself and that the fibre, rather than being a homogeneous unit element of the web, is itself a network with a void structure partially filled with water.

The significant factor I see arising from this new viewpoint is that there is no distinction between the physical properties of the intrafibre and interfibre networks or of the water they contain. Page & Tydeman, also Stone & Scallan have shown that a substantial portion of the water in a web 40–50 per cent dry is in the intrafibre voids, rather than in the interfibre voids as previously assumed. Van den Akker has shown that liquid water can be squeezed out and re-absorbed from a fibre in equilibrium with 70 per cent rh by squeezing and relaxing the fibre. At this relative humidity, the fibre contains less than 10 per cent water in all forms of association.

Vollmer and Rounsley\* have studied the permeability of paper to water vapour and, in order to explain the anomalous behaviour of water vapour in contrast to other gases, postulated condensation of the water vapour on to the cellulose and that the increased transmission rate of the water through the sheet was within this condensed liquid phase. By thermodynamic analysis of the moisture isotherms, they were able to calculate the energy of condensation of water vapour on to the cellulose. They found an initial monomolecular layer with an energy of condensation considerably greater than for condensation of water vapour itself, but that subsequent molecular layers were formed with a condensation energy very close to that of liquid water.

Walker<sup>†</sup> has studied the adsorption of microwaves by paper and has similarly found that, below 3–5 per cent moisture content (that corresponding to near saturation of the first monomolecular level), there is very little absorption of 22 Gc/s microwaves<sup>‡</sup> (the only absorption peak of water in the microwave band and corresponding to rotation of the free molecule): but, at higher moisture contents, the incremental moisture absorbs at this frequency exactly as if it were free water.

Kurath and co-workers (Institute of Paper Chemistry) have studied the compression of fibre mats up to extremely high pressures. They found the

 $\ddagger Gc/s = Gigacycle/sec = 10^9 c/s$ 

<sup>\*</sup> Vollmer, W., Chem. Ing. Techn. 1954, 26 (2), 90-94; Rounsley, R. R., Amer. Inst. Chem. Eng. J., 1961, 7 (2), 308

<sup>\*</sup> Walker, C. W. E., 'Microwave Moisture Measurement': Proc. 5th International Pulp and Paper Instrumentation Symposium, 1964, Instrument Society of America

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same linear logarithmic relationship between pressure and concentration or mat density up to mat densities approaching  $1 \text{ g/cm}^3$ . In other words, the compressibility of the fibres, which is obviously the controlling factor at high pressures, follows the same relationship and the same proportionality constants as the compressibility of the network structure that controls at low pressures.

All these observations point to a continuum of structure and void from the macroscopic to the submicroscopic and that only at the dimension of a single molecular layer on the surface of the cellulose itself is there a differentiation. Drying consists therefore in the progressive removal of water starting with the larger pores in the sheet and continuing down the spectrum until the water is removed from pores of molecular dimensions with no difference of mechanism apparent between interfibre and intrafibre pores. Bonding and shrinkage also occur at all stages of water removal and again proceeds by the same mechanisms both in the interfibre and the intrafibre network.

Mr J. W. Swanson—What has been said about the types of water in the fibres is all very interesting, but I would like to emphasise one point that Stone has already mentioned briefly. This concerns the inability to freeze that part of the water he refers to as the microreticular water. Dr Merchant studied this problem several years ago:\* he found it impossible to freeze this water in cellulose fibres at  $-195^{\circ}$ F, then sublime it off at  $-20^{\circ}$ F. This indicates that the water is held so strongly that its colligative properties are changed in some respect.

**Dr A. H. Nissan**—I would like to continue on this point. The water in the 35 Å slit would give you something of the order of 8–10 molecules across, depending on what you take for the volume occupied by a single water molecule. If the middle layer of water is separated off, according to one of the curves shown, the slit remains at 35 Å and therefore you have a tremendous dislocation in that system. The forces tending to contract the two sides are calculable with some approximations and I believe that they will turn out to be very large indeed. Therfore, one would have to postulate a geometrically strong section—a circle, for example—to explain these compressive forces. There is something to be explained therefore in assuming that we have a flat slit that is wide and in which we have free water in a liquid state.

A second point: I hope that I am not one of those who are difficult to convince, but as easy to convince as Giertz, though I think his question was unanswered. He indicated that the void dimensions were calculated on the assumption of the geometry of a flat slit. I believe he was saying, supposing you started with another geometrical figure such as a loose porous structure of

\* Merchant, M. V., Tappi, 1957, 40 (9), 771-781

hemicellulose with lots of holes in it, what would you arrive at? Would it be circles of 35 Å radius or some other figure? In other words, are we arguing in a circle? If we are, we ought to go back and recalculate; if not, then the slit pattern of voids is a very interesting picture and a very important one that must also be related to others. For example, Page and his colleagues have indicated their belief that the bonded areas between fibres are completely hydrogen bonds with no voids. How can that be so, if voids are in fact so ubiquitous in cellulose?

There are many of these items that have to be correlated before we can fully agree, as we would like to, that the picture that is emerging is established. I find it very exciting and hope that these calculations Giertz has asked for will be made.

**Chairman**—We cannot say that we have one fraction of water directly adsorbed and all the rest unbonded water. It seems to be possible to distinguish between different degrees of bonding. This is what I had hoped that Robertson would have commented upon, because he has measurements that indicate the presence of water and that show different degrees of retention in the consolidation systems under pressure.

Dr D. A. I. Goring—Perhaps I could now comment on some recent work indicating that water is not hydrogen-bonded to cellulose. We studied the thermal expansion of cellulose: it was measured dry, also with the cellulose completely immersed in water. When wet with water, cellulose expands three times as much as when it is dry. We then measured the thermal expansion of dry glucose and of glucose in solution. To our surprise, we found that glucose appears to expand 17 times as much in water as in the dry state. It is impossible to understand this in terms of the behaviour of the glucose molecule itself. It is evidently an interaction between the molecule and water. According to the flickering cluster theory of Frank and co-workers, later by Némethy and Scheraga, water can be regarded as a two-species system-clusters of ice-like water in a matrix of unbonded water. The unbonded water has a specific gravity of 1.1 and a thermal expansion of ten times that of ice. Solute molecules dissolved in water disturb the equilibrium between the two species. For example, a hydrocarbon is a structure former-that is, it creates ice-like water on its surface. Many ions in water are structure breakers-that is, they create non-hydrogen-bonded water. Our proposal is that the polar carbohydrate surface in water breaks the water structure. This layer of broken water has a thermal expansion coefficient considerably greater than that of normal water. Therefore, the apparent thermal expansion coefficient of carbohydrate in water is greater than when it is measured dry. A further interesting point came out of this. By assuming glucose to be entirely accessible, you can calculate

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the amount of structure breaking per hydroxyl group, then compute the accessibility of cellulose on the basis of its thermal expansion. We find that cellulose is 20 per cent accessible and that the hemicelluloses xylan or glucomannan are about 100 per cent accessible. These figures are more realistic than for both wood cellulose and xylan by the tritium exchange method.

This work was reported in May 1965 at the Fifth Cellulose Research Conference held at Syracuse, N.Y. It will be published in *Journal of Polymer Science* as part of the proceedings of the meeting. The title of the paper is 'Thermal expansion of cellulose, hemicellulose and lignin' by M. V. Ramiah and myself.

**Chairman**—We have discussed whether water retained in cellulose fibres exists in the vapour or liquid phase and whether water molecules coming through a vapour phase and adsorbed by cellulose in some way give off heat that can be measured. Water in the vapour phase is not hydrogen-bonded. If it is assumed therefore that water is not hydrogen-bonded to cellulose, it remains to be explained where the heat of adsorption comes from. We can obtain good data for the heat effects, but there is still the problem of interpreting it. To me, the formation of hydrogen bonds between water and cellulose is the most reasonable interpretation.

**Prof. Giertz**—In the way the discussion has proceeded, I feel forced to draw attention to a point mentioned in my paper. It is impossible to draw any conclusions about the mechanism of a reaction from thermodynamical measurements. You can make more or less intelligent guesses about the way in which the water is adsorbed and the actual measurements may fit well with your assumption, but the model can be proved only by thermodynamical data. To know more exactly how water is sorbed by cellulose materials, we have to use other techniques such as treatment with labelled atoms.

Dr Stone—A recent paper\* showed that fibres dried by the evaporation of water and fibres dried by solvent exchange have the same heat of wetting, even though the surface area as measured by nitrogen adsorption differs a hundred-fold. They conclude from this that water does not recognise a surface in cellulose. In this sense, cellulose is similar to sulphuric acid. Analogies must not be carried too far, however; if one compares the behaviour of drops of sulphuric acid added to water with the addition of fibres to water, the difference between the two systems is obvious. The fibres remain intact, with water between them. The same can be true of structural elements within the cell wall.

\* Gregson, J. and Levi, A. A., J. Polymer Sci., 1963, Part A (1), 3 333-3 342

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**Dr H. K. Corte**—I would like to recall two facts reported in the literature— 1. The entropy of adsorption at the very beginning of the adsorption process was found to be the same as the melting entropy of ice. This indicates that the first adsorbed water molecules are in a state of order similar to that of ice.

2. The mechanism of the water vapour transmission through paper is mainly one of surface diffusion. The surface diffusion does not start until the first layer of adsorbed water molecules is completed (at about 4.5 per cent adsorbed water). This shows that the first layer is so firmly bonded to the cellulose that it is practically immobilised. Further layers become more and more mobile: they slide over each other. The surface diffusion coefficient is proportional to the number of layers and this explains the increase in water permeability of paper with increasing moisture content.

**Dr Goring**—It seems quite certain that a carbohydrate surface immersed in water is solvated. The question is this: is the water hydrogen bonded to its surface? I think we should consider here whether or not water is held to an immersed cellulose surface in the ice-like low density form that is found in Frank's flickering clusters.

**Dr** Nissan—We do not define hydrogen bonding by the structure of ice: it exists by itself and has its own criterion, totally independent of the structure of ice. We recognise it by many tests such as infra-red spectroscopy, which shows that in cellulose there is a shift in certain well-known frequencies. The important point is that we cannot define hydrogen bonds by ice structure, which in any case exists in many structures. There are six types of ice under different pressures. Which structure is the defining structure for the hydrogen bond? Then, too, there are all sorts of liquid water structure in all sorts of proportions. Many people have calculated the amount of water in ordered states and there are many theories. As a matter of fact, the whole field of water, which was clarified by Bernal some years ago, has now been thrown into confusion again, because so many other structures have come to light.

**Dr Corte**—Water is indeed known to exist in several states. Ice VI exists at 20°C under a pressure of 9 000 kg/cm<sup>2</sup> and has a higher density than ice I. The first parts of water adsorbed on cellulose have a density higher than 1; according to some workers, it can be as high as 2. When you fill a pint glass with sawdust, you will be surprised to find that you can pour in more than one pint, up to  $1\frac{1}{2}$  pints of water.