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INFLUENCE OF DRYING ON THE PORE STRUCTURES OF THE CELL WALL

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Synopsis—Using a recently proposed concept of cell wall structure based on a multiplicity of lamellae coaxial with the cell, the effect of drying on the structure of the cell wall of bleached spruce sulphite tracheids has been examined by means of nitrogen adsorption. The data suggest that in the fully water-swollen wall there are up to several hundred lamellae, each of the order of 100 Å thick, with a median separation of about 35 Å. During drying, the lamellae draw together progressively into thicker and thicker aggregates, decreasing the total pore volume, but leaving approximately the same median separation in the spaces that remain. At dryness, the pore volume remaining in the wall is negligible.

During drying, the first pores to close do not reopen when the fibres are treated with water, whereas the pores that close during the later stages of drying do so. The lamellae separation after drying at 25°C and reswelling remains at a median value of about 35 Å, but it drops after drying at 105°C and reswelling to 25 Å, owing to a greater permanency of pore closure in the pores of larger size. It is tentatively suggested that a fibre dries radially inwards towards the lumen and that the pores that tend to remain closed after drying are located towards the outside of the fibre, whereas the pores that reopen easily upon rewetting after drying are located towards the lumen.

Fibres of very different composition, chemical treatment and morphology, as well as native and regenerated cellulose fibres, possess a wide range of pore volumes, yet are shown to have very similar pore size distributions and it is suggested that this distribution is not therefore of biological origin, but is based on a property of the cellulose molecule. No obvious correlation was found between the fractional extent of irreversible pore closure upon drying and the composition of the fibres.

In the swollen cell wall of spruce sulphite pulp fibres, which contain almost 1 cm^3 water per gram of dry material, about 20 per cent of the water is present in macroreticular pores (spaces between lamellae) and 80 per cent in micro-reticular pores (spaces within lamellae). This ratio persists throughout the drying cycle.

The relationship between cell wall porosity and the papermaking properties of fibres is discussed briefly in terms of the loss of porosity during drying and its regain during beating.

Water and the fibre

THE shrinkage of paper during drying and the dimensional instability of a dried sheet under conditions of changing relative humidity is a response to the swelling and shrinkage of the individual fibres. This relationship between the dimensional changes of a sheet and those of the constituent fibres has become rather well understood in recent years, due particularly to the work of Page & Tydeman;[1] but much less well understood are the changes taking place within the fibres themselves that cause them to swell when water is added to them and shrink when it is evaporated. At first sight, the system seems simple enough—water added to a dry fibre increases the volume of the fibre by an amount that is very approximately the volume of the water added, so swelling can be seen as the entry of water into the cell wall, causing the separation of structural elements within the wall; shrinkage is seen as the reverse of this process. The exact manner in which water is accommodated within the cell wall is, however, far from clear and it is the purpose of the present paper to examine this question in some detail. The discussion will, in general, be restricted to native cellulose fibres and refer particularly to the tracheids of softwoods, but certain aspects of it are pertinent to cellulose fibres in general, including those of regenerated cellulose.

There are three possibilities for the accommodation of water within the cell wall. Firstly, it could enter capillaries already present in the dry fibre. Secondly, it could form capillaries or pores by separating surfaces that were previously joined. Thirdly, it could form a molecular association with the cell wall components—in effect, dissolving in them—with the production of no real surfaces. These three possibilities will be examined separately.

Pores present in the dry cell wall

THE existence of pores within the cell wall of dry cellulose fibres, into which water may enter when the fibre is wetted, has been demonstrated in several ways. Dry fibres of cellulose, both regenerated and native, have been shown to give a diffuse low angle scattering of X-rays, which has been interpreted as due to the presence of microvoids.[2,3] The size of the voids measured in this way lie in the range 20–300 Å in radius and their volume in the case of ramie amounted to 0.5 per cent.[3]

The volumes of pores up to an equivalent radius* of 300 Å has also been

* Although the term *radius* will be used to define pore size, this term applies only to cylindrical pores. In the case of slit-like pores (which will be described later), *radius* is replaced by *wall separation*

determined by adsorbing nitrogen on to the sample at −195°C and applying the Kelvin equation to the sorption isotherm in the region of high partial pressures, where liquid nitrogen condensation within the pores is presumed to occur. By this means, a bleached spruce sulphite pulp dried from water at 105°C was found to have a pore volume of 0.2 per cent.[4]

Both the nitrogen adsorption and the X-ray methods are limited to determining the volume of pores not more than 300 Å in radius; if the examination of the cell wall is restricted to these two methods, therefore, nothing can be said about the presence or absence of pores larger than 300 Å. The volume of pores up to several microns in diameter can be measured, however, by the mercury intrusion technique and, when this method was applied to dry bleached spruce sulphite fibres, it was found that the volume of pores smaller than 0.3 micron was less than 0.02 cm^3/g.[33] Any pores in the cell wall larger than this should be readily visible microscopically, but optical and scanning electron micrographs taken by us have failed to reveal any such gross pores.

Conflicting evidence has been reported from microscopic measurements of the cell wall density of fibres dried from water.[5,6] In these methods, the cell wall density was determined from the weight per unit length of fibre and the microscopically determined fraction of the cross-sectional area of the fibre that is cell wall. Reported densities obtained in this manner are 0.95–1.10 g/cm^3 for cotton[5] and 0.88–1.08 g/cm^3 for various softwood pulp fibres.[6] These densities of about unity suggest up to 0.36 cm^3/g of pore volume. It is considered, however, that this microscopic method must contain a considerable error.[4]

Summarising, the existence of pores within the cell wall of dry native cellulose fibres has been demonstrated in a number of independent ways. The volume of such pores is likely to be small, however—probably appreciably less than 0.02 cm^3/g—and should have little influence on the relationship between water uptake and the resulting change in cell wall dimensions.

Formation of pores during swelling and loss during drying

ALTHOUGH the opinion has been expressed a number of times[7–9] that the addition of water to dry cellulose is a bulk phenomenon, equivalent to a solution process and that it is no more reasonable to discuss the presence of internal surfaces than it would be in the case of water being added to, say, sulphuric acid, it is relatively simple to demonstrate that real surface *is* produced when water is added to dry native cellulose fibres.

If cellulose fibres are swollen in water, then treated by a succession of progressively less polar solvents and the final solvent evaporated in a stream of dry gas—a process known as solvent exchange drying—the material is found by nitrogen adsorption measurement to have a very large specific

surface.[10–17] The area of this surface is two orders of magnitude greater than that of the original dry, unswollen material, showing that swelling in water created surface that was recognisable as such by the nitrogen molecule. The surface created is so much greater than the increase in external surface of the wall that it must be contained within the wall itself, presumably as the surface of pores that were produced by the separation of structural elements as water entered. These pores are evidently of a size sufficient for the water that enters them to exhibit the same properties as bulk water, in that it is able to mix with the first solvent used in the solvent exchange procedure.

A word should be said about nitrogen adsorption as a technique for studying pore structure. Measurements are made at −195°C and the volume of nitrogen adsorbed at various partial pressures of nitrogen used to plot an adsorption isotherm. Analysis of this isotherm in the region of partial pressures between 0.05 and 0.35 by the BET method[18] permits the calculation of total surface area accessible to the nitrogen molecule (diameter 3.6 Å). Analysis of the isotherm at higher partial pressures of nitrogen by the Pierce method[19] permits the calculation of total pore volume (up to about 200 Å radius) and distribution of volume and surface amongst pores of all sizes up to about 300 Å radius.

The method has been applied to native cellulose fibres by several workers[4, 10–17] and there is general agreement on the following points—

(*a*) The specific surface area of fibres dried from water is about 1 m^2/g.
(*b*) The specific surface area of water-swollen fibres dried by solvent exchange is many times greater than 1 m^2/g, values ranging up to 200 m^2/g.
(*c*) The pores that are responsible for the large surface area of swollen fibres are small, the most common pore size being of the order of 16–22 Å radius and the median pore size (that size above and below which exists 50 per cent of the total volume) is about 35 Å.

The translation of these data into a physical picture of cell wall structure is clearly an important objective of these measurements, but, surprisingly enough, few attempts at such an interpretation have been made. Possibly one of the reasons for this is that nitrogen adsorption gives a great deal of quantitative information on the *size* of pores and particles, but little or none on their *shape* and to formulate a structure, it is necessary to have both. For convenience, in the calculation of pore size distributions from the sorption isotherms, pores are assumed to be cylindrical and the size then appears as a radius, but this is not to be taken as meaning that the pores are, in fact, cylinders with rectilinear walls. Using the cylindrical model, it has been suggested[16, 18] that the most common pores in swollen cellulose, with a measured 'radius' of 16–22 Å, may be the spaces between hexagonally packed microfibrils of 230 Å diameter. One of the difficulties with this model,

however, is that it does not provide a mechanism for the almost complete loss of pore volume that occurs when a water-swollen fibre is dried. In order to correct this and other deficiencies in such a model, we have proposed an entirely different structure for the cell wall.[4] This proposal was based on microscopic evidence obtained over the course of many years by botanists and others, the literature on which has been reviewed by Roelofsen;[20] on concepts described by Emerton[21,22] in connection with the beating of wood-pulp fibres; and on our own study of wall structure by means of nitrogen adsorption and electron microscopy. As this model is necessary for describing the formation of pores during wetting and loss during drying, it will be reviewed briefly at this time.

The multi-lamella concept

IT is postulated that, within the cell wall, microfibrils rectangular in cross-section are associated laterally to form sheets. These sheets are arranged coaxially to the fibre and may aggregate into thicker sheets or lamellae, the average thickness of which depends upon the extent to which the fibre is swollen. A fibre dried from water has a single lamella, the whole cell wall, whereas a completely swollen fibre consists of several hundred spaced lamellae. The progressive swelling and its reversal—progressive drying—of the cell wall is illustrated in Fig. 1.

According to this model, the pores measured by nitrogen adsorption are the spaces between lamellae and are slit-like; the large surface area observed with swollen fibres is due to the multiplicity of surfaces presented by the separation of lamellae. The thickness of the lamellae and their number in a cell wall may be derived quite simply. For a lamella of any non-porous material, for which the thickness is small compared with the other dimensions, the following relationship holds—

$$t = 2V/A \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where A is the specific surface area, V is the specific volume and t is the thickness.

If a dry fibre is considered to be a single lamella of cellulose in the form of a tube and the wall thickness is the lamella thickness, it is thus possible, by measuring the specific surface of unbonded, water-dried fibres, to calculate the average thickness of the cell wall. The specific volume of cellulose is 0.64 cm^3/g and a reasonable value for the specific surface of unbonded, water-dried spruce tracheids is 1 m^2/g,[4,10–17] so from equation (*1*) the wall thickness should be 1.28 μ. Microscopic examination of spruce tracheids shows the average wall thickness to be 2–3 μ. The agreement, already good, is made even better by taking into account the surface roughness of the tracheid walls. To

make the agreement exact, a roughness factor of about 2 would be required—a not unreasonable value.

For a surface area of, say, 100 m^2/g, such as might be obtained with a swollen fibre, substitution in equation (*1*) gives a lamella thickness of 128 Å. Since the same fibre when dried from water would have a cell wall thickness of

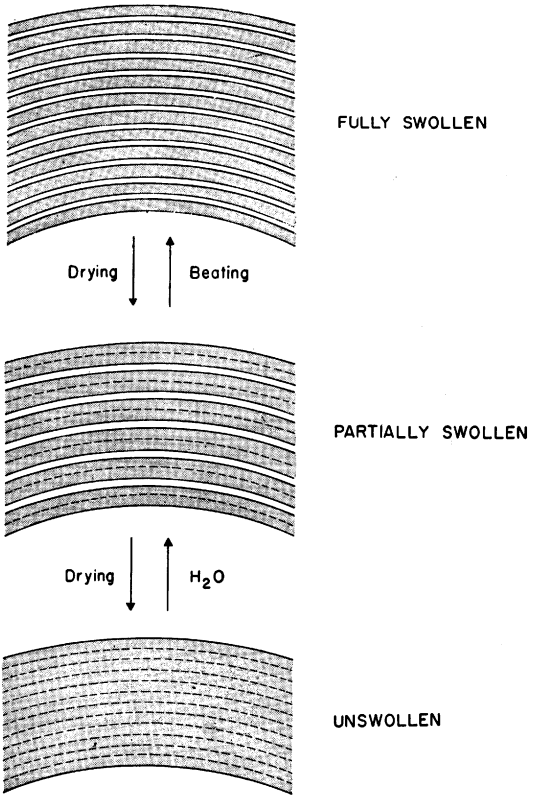

Fig. 1—Simplified diagram of a drying/reswelling cycle

1.28 μ, this figure of 1.28 μ divided by the lamella thickness of 128 Å gives the number of lamellae in the swollen cell wall as 100. The numerical coincidence of the surface area (in m^2/g) with the number of lamellae results from the choice of 1 m^2/g as the surface area of a fibre dried from water rather than, say, 0.8 or 1.2 m^2/g.

These calculations are based on an assumption that the cell wall of the dry fibre is non-porous, which is a fair approximation, if the pores amount to less

than 2 per cent of the solid volume. It is assumed also that the various morphological layers P, S1, S2, etc. form a continuum in the water-dried fibre.

Since the solid material of the cell wall in the swollen fibre is considered to be built up of parallel lamellae, then the pores between these lamellae must be parallel-sided slits. All calculations based on cylindrical pores—the Kelvin equation used in the Pierce analysis[19] and Washburn's relationship used in the mercury penetration method,[23] etc.—are still valid, although it can be shown that pore width now must be substituted for pore radius.[24,25]

Application of multi-lamella concept to drying

IN the multi-lamella concept, we have described the swelling of the cell wall as the progressive separation of the practically solid cell wall into thinner and thinner lamellae not in superficial contact. If a dry fibre is immersed in water, then the pores developed between the lamellae must fill with water as they are created. Drying from water may be regarded as the reversal of swelling in that the receding water closes the pores, leaving the dry cell wall as a continuum containing very few, if any, pores. Although this mechanism describes the entire process in a qualitative way, it is of considerable interest to examine the system quantitatively by asking, for example—

1. At what moisture content is the cell wall completely swollen—that is, at what moisture content does shrinkage of the cell wall commence upon drying?
2. How does the average pore size and pore size distribution in the cell wall change during drying?
3. There is known to be a reduction in the extent to which a fibre may be swollen after it has been once dried from water. Is the irreversible pore closure associated with pores of a certain size or are all pores involved?
4. How does pore structure and drying behaviour vary with the nature of the fibre (method of preparation, chemical composition, etc.)?

In order to answer these and related questions, a commercial bleached spruce-balsam sulphite pulp was obtained from a mill in a never-dried condition. Samples of this pulp were made into bulky pads while retaining as much water as possible. The first of these pads was placed in a sample tube, which was then filled with water and left overnight to ensure that the pad was completely swollen. The sample was then solvent exchange dried by displacing the water with dry methanol, displacing the methanol with dry pentane and, finally, by evaporating the pentane at 25°C in a stream of dry nitrogen. A number of samples were dried at 25°C to different moisture contents and the residual moisture removed by solvent exchange, as described above. Finally, a further series of samples was dried at 25°C to different

moisture contents and then reswollen in water by filling the sample tube with water and leaving overnight before solvent exchanging. Thus, we were able to preserve the structure of the fibres in a never-dried condition, in a partially dried condition and in a partially dried and reswollen condition. Nitrogen adsorption isotherms were determined on all the samples and a complete analysis of each made by the BET method and the Pierce method. The data on these samples are collected in Tables 1 and 2 and shown graphically in Fig. 2–4.

TABLE 1—POROUS STRUCTURE AT VARIOUS STAGES OF DRYING AT 25°C

Water present before solvent exchange drying		*Specific surface, m^2/g*		*Pore volume, cm^3/g in pores to 300 Å*	
*per cent**	*cm^3/g*	*BET*	*Pierce*	*Experimental***	*Pierce, ΣVp*
95	20	93	—	0.160	—
64	1.78	93	109	0.160	0.176
67	0.89	89	104	0.155	0.156
42	0.725	65	69	0.120	0.120
28	0.39	51	54	0.080	0.075
24	0.315	51	46	0.068	0.064
13	0.15	24	22	0.033	0.030
4	0.04	7	—	0.007	—
0	0.00	1	—	0.002	—

TABLE 2—POROUS STRUCTURE DEVELOPED AFTER PARTIAL DRYING AT 25°C AND RESWELLING IN WATER

Water to which fibres reduced before reswelling, per cent*	*Specific surface, m^2/g*		*Pore volume, cm^3/g in pores to 300 Å*	
	BET	*Pierce*	*Experimental†*	*Pierce, ΣVp*
48	83	89	0.150	0.150
47	80	93	0.158	0.162
42	87	93	0.145	0.145
37	75	73	0.131	0.128
28	59	57	0.100	0.100
24	51	57	0.088	0.087
15	52	46	0.090	0.084
13	53	51	0.083	0.080
4	55	55	0.080	0.076
0	55	—	0.080	—

* Percentage water calculated as (weight of water × 100)/(weight of solids + water)
† Volume of nitrogen (in cm^3 liquid) sorbed by the sample at $P/P_0 = 0.965$

Examination of Fig. 2 reveals that very little happens on drying from very high moisture contents until a value of about 50 per cent (equal parts of

water and fibre) is reached. At this point, which is close to the critical moisture content at which Robertson[26] has found a number of physical properties of fibres and fibre networks to change, the pore volume starts to decrease and continues to decrease to zero moisture, at which point the pore volume has also been reduced virtually to zero.

The curve obtained after reswelling the partially dried fibres is revealing. In the region of high moisture content, between 50 and 30–40 per cent water, the pores that are lost during drying are not recoverable by soaking in water. As drying is continued below the 30–40 per cent moisture level and more and

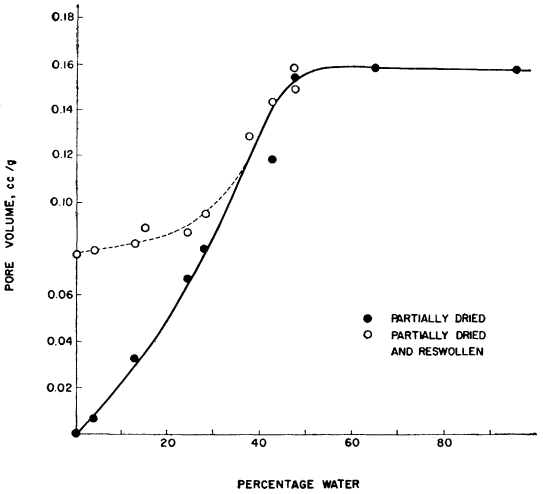

Fig. 2—Change of pore volume during drying

more pores close, however, it is found that some of these pores can be re-opened by soaking in water. It is seen that the volume of the pores obtained after reswelling remains almost constant from the 30–40 per cent moisture level down to complete dryness and it follows therefore that the volume of the pores that remain irreversibly closed also remains constant during this part of the drying cycle.

There would therefore appear to be two sorts of pore in the cell wall of these fibres. One sort, which represents approximately half the total volume of the pores (0.08 cm^3/g) close irreversibly during drying, commencing at about 50 per cent moisture and being more or less completely closed at 30–40 per cent moisture. The other sort, representing the other half of the total volume, start to close in the 30–40 per cent moisture region and continue to

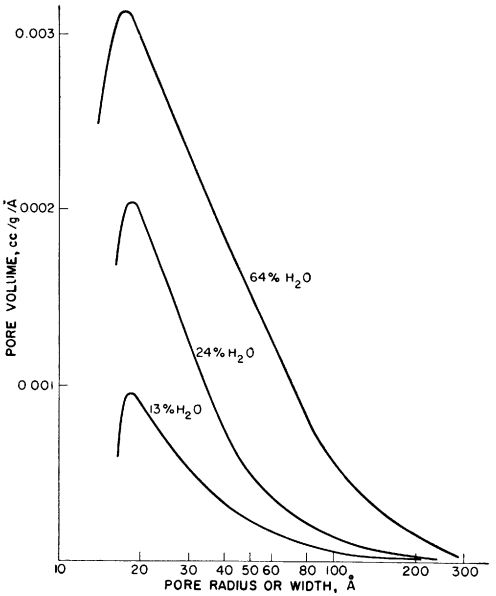

Fig. 3—Pore volume distribution curves of bleached spruce sulphite pulp solvent exchange-dried at different moisture contents: distributions calculated from the adsorption branch of the adsorption/desorption isotherm

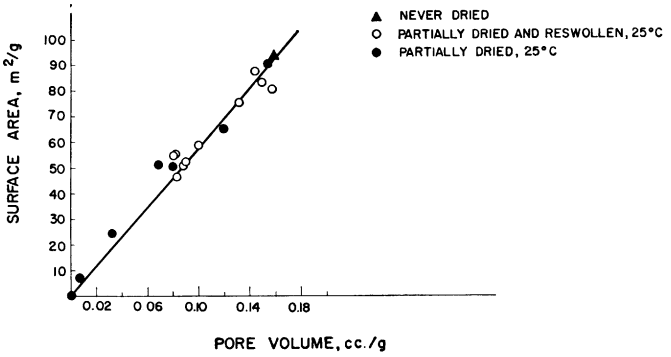

Fig. 4—Surface area/pore volume relationship for a bleached spruce sulphite pulp

close right down to complete dryness, but all these pores can be reopened by a simple swelling treatment with water.

Examination of the pore size distribution curves in Fig. 3 reveals that the difference between the reversibly and irreversibly closing pores is not based on size. At each stage of dryness, the pore size distribution remains approxi-

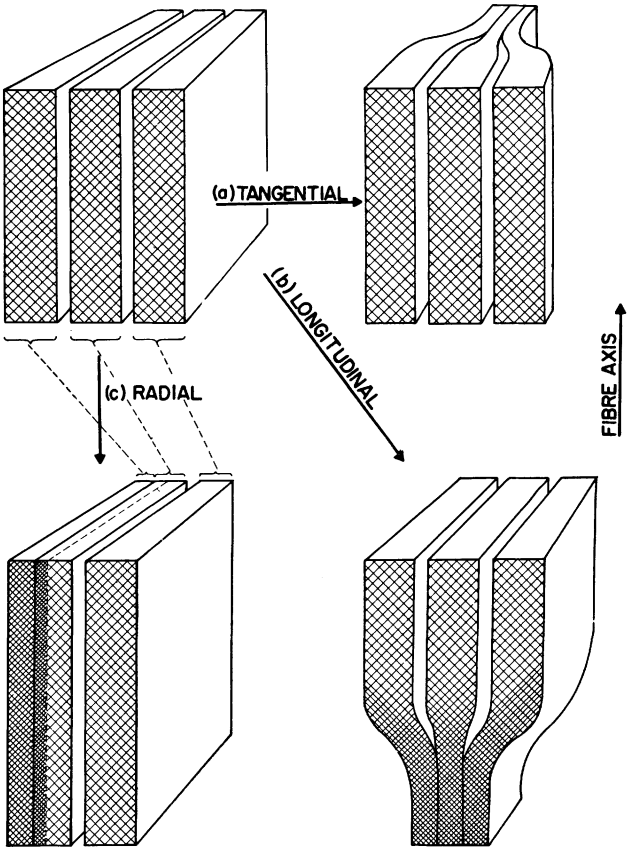

Fig. 5—Possible modes of pore closure

mately the same. This is shown in a different way in Fig. 4, in which the surface area is plotted against the void volume at various stages of drying. All points fall on a straight line passing through the origin, showing that the median pore size ($2V/A$) remains constant. Its value, obtained from the slope of the line, is 35 Å. The pictorial representation of this must be purely hypothetical at the present time and three possibilities are sketched in Fig. 5.

In this illustration and in much of the discussion to follow, the existence of a distribution of pore sizes as shown in Fig. 3 is tacitly ignored and the median pore size used as a convenient average. The reasons for adopting this course are based partly on the unwieldiness of dealing with a distribution of sizes, but largely because the source of the variation that leads to the distribution shown in Fig. 3 is unknown. Continuing the examination of Fig. 5, a pore might close progressively from one side or from one end (Fig. 5*a* and *b*), thereby maintaining the same volume/surface relationship. A similar mechanism was proposed by Hunt, Blaine & Rowan.[12]

Alternatively—and more likely—drying could cause lamellae to move together and the spaces between them close completely, one after another, radially inwards from the exterior of a fibre towards the lumen. Pores would thus be either completely open or completely closed, except in the transition zone, which, if narrow enough, would be insufficient to affect the distribution of pore sizes. In support of this pattern of drying (illustrated in Fig. 5*c*), Hermans[27] reports that the reverse process—the moistening of a dry rayon filament—proceeds radially inwards, a sharply defined moistened mantle being formed at the periphery of the fibre, which gradually thickens, the core of the filament retaining its initial moisture content. This sharp line of demarcation between the dry core and the already moistened mantle, which moves gradually inwards, can be readily seen under the microscope. In view of this, it seems possible that the drying of a wet fibre proceeds in a like manner.

Further support for this mechanism has been provided recently by Greyson & Levi.[28] Starting with water-swollen cotton fibres dried by solvent exchange, they measured the specific surface by nitrogen adsorption, treated the fibres with a small amount of water vapour, evaporated the water and remeasured the specific surface. It was lower than the initial value, owing to the wetting of certain pores and closure during evaporation. When moisture was added to this material a second time and the evaporation and surface area measurement repeated, it was found that no further surface was lost until the second addition of water exceeded the first. In other words, when water is added to fibres in which the pores have been partially collapsed, it enters the same region as before (the region of collapsed pores) and does not enter the region of uncollapsed pores as might have been expected. The simplest explanation for this behaviour is that water vapour added to fibres dried by solvent exchange enters first the periphery of the wall and forms a mantle of moisture that, when evaporated, produces a mantle of non-porous cell wall material. When water is added a second time, it necessarily saturates first the same material that it did on the first occasion and only when an amount of water greater than that added on the first occasion has been added to the fibre does the moisture mantle move radially further towards the lumen.

Based on this model, it appears that the pores to close *irreversibly*—an event in the early stages of drying—must be located towards the outside of the cell wall. Similarly, the pores to close *reversibly*—an event during the later stages of drying—must be located towards the inside of the cell wall adjacent to the lumen.* No explanation can be given for this behaviour, but it may be speculated that the stresses to which the cell wall is subjected as a result of shrinkage of the outer lamellae prior to shrinkage of those near the lumen are to some extent responsible.

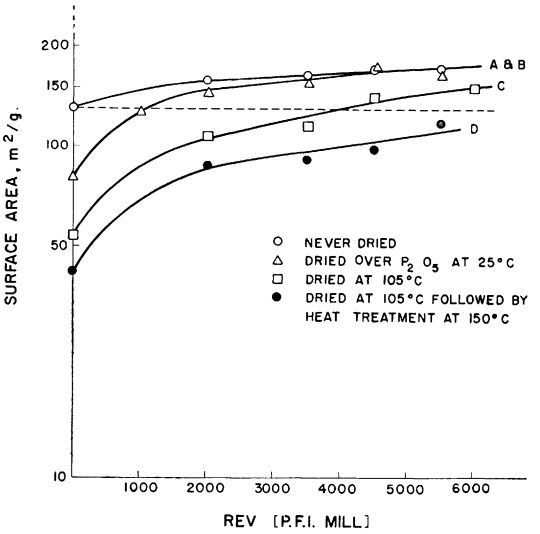

Fig. 6—Influence of beating on the specific surface of pulp dried at several temperatures

Opening of pores by beating

THE bleached spruce sulphite pulp used for the main part of this study was dried in several ways (described below) in order to produce pore closure, soaked in water at 25°C (causing a partial reopening of pores) and the pulps then beaten in PFI mill to see whether the remainder of the pores could be reopened by mechanical means. The result shows (Fig. 6) the change in porosity with degree of beating in terms of total specific surface area. The never-dried pulp is seen to be affected somewhat by mechanical treatment, the surface area (and therefore, according to the multi-lamella concept of

* It is assumed that the pits are too small to permit drying to take place from the lumen side of the wall. If drying and wetting *can* occur from the lumen side, the centre of the wall will constitute the point furthest from the external environment

structure, the number of lamellae) increasing 30 per cent as a result of 5 500 rev in the beater. Drying the pulp at room temperature over phosphorus pentoxide to a nominally zero moisture content closes a number of pores that do not reopen on simple soaking, but these are seen (Fig. 6, curve B) to be completely reopened by beating for a short time (1 000 rev). Further beating gives the same increase in surface as that experienced by the never-dried pulp. Drying at 105°C for 1 h or at 105°C followed by a 1 h heat treatment at 150°C leads to the results shown in Fig. 6, curves C and D. Drying at 105°C causes

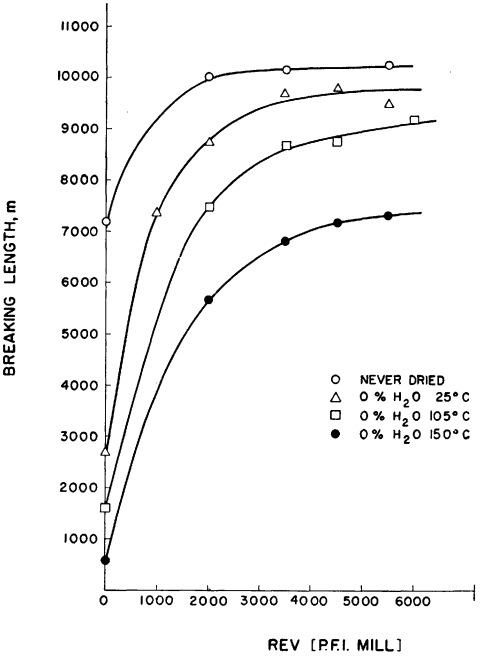

Fig. 7—Influence of beating on the breaking length of pulp dried at several temperatures

a loss of porosity such that it now requires 4 000 rev in the PFI mill to return it to the original never-dried state, but extended beating never produces the internal surface realisable by the never-dried pulp. The heat treatment at 150°C took this permanent irreversibility of pore closure even further.

The influence of these changes on the papermaking properties of the pulp is shown for breaking length in Fig. 7 and the similarity between this and the previous set of curves (Fig. 6) is obvious, though it is not intended to suggest from this that the papermaking properties of a pulp are related quantitatively

to the total surface area of the pulp. Clearly, there are many other factors that determine the properties of paper—among others, the cross-sectional shape of the fibres, the distribution of fibre lengths and the extent of external fibrillation—all quantities that will not materially affect the very large total surface, which is measured by nitrogen adsorption on solvent-exchange-dried fibres. Qualitatively, however, it may be said that, when a bleached spruce sulphite pulp is subjected to a drying treatment that causes a loss of total surface, which cannot be regained by beating (or other means), the pulp will make a weaker sheet of paper. Furthermore, experiments not described here show that, if a never-dried pulp and the same pulp dried at 25°C are beaten for different times such that both their total surface and fibre length distribution are the same, the sheet properties are found to be identical. The total surface area therefore is an important quantity, in that it measures the number of lamellae into which the cell wall has been divided and the flexibility of the wall should increase as the square of this number.[4] This we consider to be the true meaning of the expression *internal fibrillation*, which has been used so frequently in the past. Thus, for sheets of high tensile strength and large bonded area, when the flexibility and conformability of fibres must be at a maximum, the total specific surface as measured by nitrogen adsorption must also be a maximum.

Examination of various fibres

THE work described to this point has been concerned with a bleached spruce sulphite pulp. In order to examine the influence, if any, that the composition of the fibre has on its porosity and drying behaviour, a variety of samples was examined in the never-dried state, also after drying at 105°C for 1 h and resoaking in water for 2 h. The materials dried by solvent exchange were subjected to a complete pore analysis (Table 3). The materials included bleached and unbleached kraft and sulphite pulps from spruce, a spruce alpha-cellulose, hollow filament rayon* and a spruce groundwood fraction. Notwithstanding the considerable difference in composition, the pore size distribution curves (not shown) were all very similar, even for the hollow filament rayon and suggest very strongly that the pores in native fibres have a distribution of sizes that is not biologically controlled, nor a function of chemical treatments, but rather is based on some property of the cellulose molecule that causes it to aggregate into certain preferred arrangements.

In Fig. 8, the pore volume is plotted against the specific surface for the pulps discussed above, as well as for the bleached spruce sulphite pulp at

* The hollow filament rayon was obtained in the dry state from American Viscose Corpn., Marcus Hook, Pa. A never-dried solid filament rayon was examined, but it proved intractable because of the very long times required for nitrogen sorption equilibrium

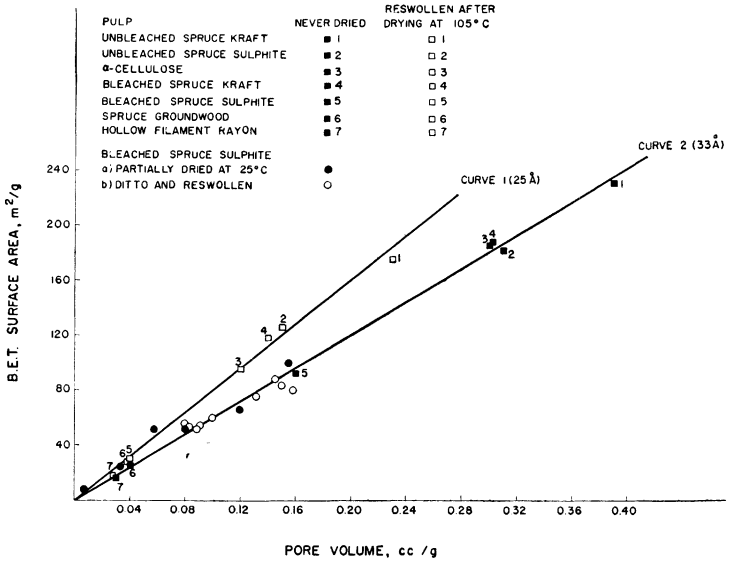

Fig. 8—Surface area/pore volume relationship for various pulps

TABLE 3—PORE ANALYSIS OF VARIOUS PULPS

Description of sample	*Never-dried*			*Dried at 105° and reswollen*[3]			*Extent of surface recovery, per cent*
	Specific surface,[1] *m^2/g*	*Pore volume,*[2] *cm^3/g*	*Median pore size (2V/A), Å*	*Specific surface,*[1] *m^2/g*	*Pore volume,*[2] *cm^3/g*	*Median pore size (2V/A), Å*	
Unbleached spruce kraft	230	0.39	34	175	0.23	26	76
Bleached spruce kraft	185	0.30	32	118	0.14	24	64
Unbleached spruce sulphite	182	0.31	34	125	0.15	24	69
Bleached spruce sulphite	93	0.18	39	30	0.04	26	32
Spruce alpha-cellulose	185	0.30	32	95	0.12	25	51
Hollow filament rayon[4]	16	0.03	37	16	0.03	37	100
Spruce groundwood, 14/28 fraction	26	0.03	23	25	0.04	32	96

1. BET method
2. Up to 300 Å pore separation
3. Dried at 105°C for 1 h: reswollen in water at 25°C for 2 h
4. Supplied by American Viscose Corporation in the dry state

various stages of drying, shown previously in Fig. 4, the data for which are included for the sake of comparison. It is seen that all the points fall close to two straight lines passing through the origin, one line being characteristic of the never-dried samples and those partially dried at 25°C or partially dried and reswollen; the other being characteristic of the samples dried at 105°C and reswollen. The slope of the line is a measure of the median pore size, which for the never-dried and partially dried (at 25°C) fibres is about 35 Å and for the fibres dried at 105°C and reswollen is about 25 Å. Since all the

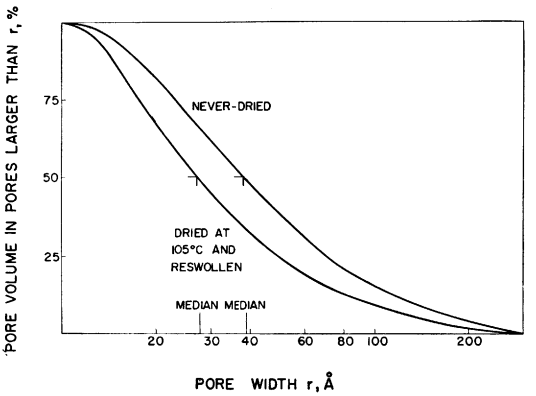

Fig. 9—Cumulative pore volume curves calculated by the Pierce method illustrating the change in distribution of pore volume with drying at 105°C and reswelling (alpha-cellulose woodpulp)

various pulps fall on these two lines, their median pore sizes are similar before drying and change in a similar way as a result of drying at 105°C. The hollow filament rayon and spruce groundwood fibres have slightly anomalous values of median pore size (Table 3), probably due to inaccuracies in measuring the very small pore volumes existing in these samples; yet, considering the differences between such samples and the chemical wood pulps, the agreement between them is reasonable.

The shift to a lower value of median pore size when the samples are dried at an elevated temperature and reswollen in water is due to a more permanent closure of the pores of larger size. This is shown for the spruce alpha-cellulose pulp in Fig. 9. The effect may be considered to result from an inelastic deformation of the pores as they close during drying, an effect that would be more likely in the larger pores and the change from an elastic to a plastic

deformation would be promoted by high temperatures because of the thermally induced motion of microfibrils.[29] This suggested mechanism corresponds to the stress relaxation in dried fibres caused by a rise in temperature, discussed by Robertson.[30]

The degree of permanency of pore closure, as indicated by the extent of surface recovery, is seen from Table 3 to be unrelated in any obvious manner with chemical composition. The only fibres that seem to be unaffected by drying at 105°C are spruce groundwood and hollow filament rayon, two materials of very dissimilar composition. There is some indication that bleached pulps, when dried, are less easily reswollen than the same pulp before bleaching, but it is very clear that factors other than composition are involved in the permanency or otherwise of the pore closure and shrinkage of a fibre when it is dried. This was confirmed by many experiments in which the composition of a fibre was varied systematically by the progressive extraction of a single component. Thus, 70 per cent of the lignin in a groundwood pulp was removed by sodium chlorite treatment, but little change occurred in the reversibility of pore closure. A similar lack of response to changing composition was observed when xylan was extracted with sodium hydroxide from a bleached hardwood kraft pulp containing 26 per cent pentosans. In neither case was all the lignin or all the xylan removed.

Such negative results are rather unsatisfactory, but they have the virtue of demonstrating that no simple explanation for variations in irreversible pore closure can be given based on properties attributable to lignin or hemicelluloses. There is therefore clearly a need to seek alternative or additional explanations.

Molecular porosity

FROM Table 1, it can be seen that the pore volume measured at any stage of drying is considerably less than the volume of water present. At low moisture contents, the pore volume is a constant fraction (one fifth) of the water present. If the remaining four fifths water is not in the pores, it must be present in the 'solid' lamellae as gel or molecularly bound water and is removed during solvent exchange without leaving pore space. These pores in the solid, which exist while water is present, might be classified as microreticular pores in contrast to the macroreticular pores that can be measured by nitrogen adsorption.[31]

In Fig. 10, the pore volume is compared with one fifth of the volume of the water present. The two correspond closely below about 50 per cent water; above this percentage, the macroreticular pore volume is approximately constant. This may be interpreted as follows. While the sample is above cell wall saturation (about 50 per cent), drying results in a loss of free water only.

As drying progresses below the saturation value, the ratio of the water lost from the micro- and macro-reticular pores remains constant. Thus, in terms of what has already been proposed, as the macroreticular pores close, water simultaneously diffuses out of the adjacent lamellae. If it is assumed that the water in the lamellae adds approximately its own volume to the volume of the solid material present, then drying should result in a thinning of the

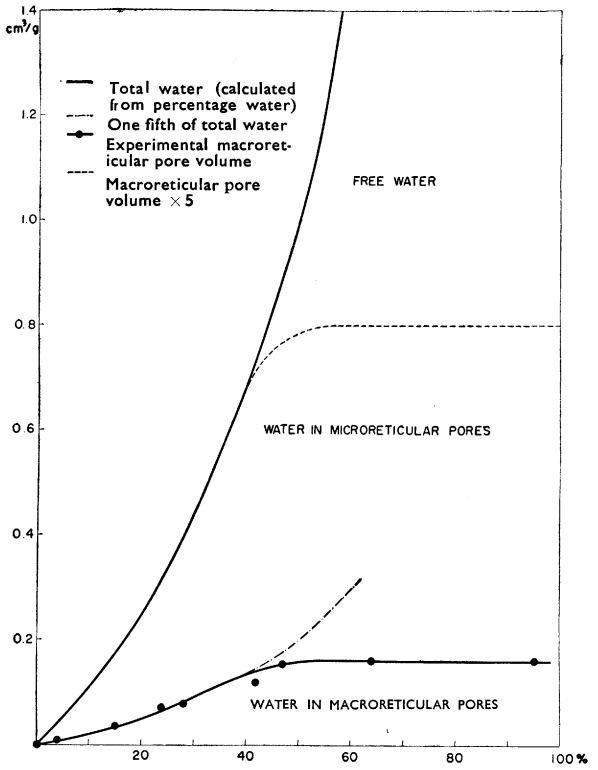

Fig. 10—The distribution of water between macroreticular and microreticular pores in a bleached spruce sulphite pulp

lamellae. For this reason, we have drawn the dried-out lamellae in Fig. 5 thinner than those that still border uncollapsed pores.

The ratio of 1:4 for the ratio of the macro- to the micro-reticular pore volume corresponds approximately to the ratio of the pore width to the lamellae thickness. Presumably, if a sample of higher initial surface area than

the bleached spruce sulphite fibres had been used, the lamellae would have been thinner and the macroreticular pores would have represented a higher fraction of the total swollen pore volume.

Water in the swollen cell wall of native cellulose fibres is thus largely in the form of a molecular association with the cellulose, in agreement with the analogy that has been drawn so frequently between the addition of water to cellulose and the addition to sulphuric acid. The analogy is quite wrong, however, in considering that all the water in the cell wall is held in this way. Cellulose is a solid, not a liquid and has structure and rigidity. It should therefore be inherently capable of containing channels of any size and, by means of solvent exchange and nitrogen adsorption, this capability has been shown to be a reality. The very large amount of water not contained within the macroreticular pores is clearly very important from the viewpoint of dimensional changes occurring during drying and wetting, also when considering the movement through the cell wall of solvents other than water and solutes dissolved in water. The apparent inability of non-polar solvents to penetrate the microreticular pores means that these will close during solvent exchange drying and the matrix in which they were contained will shrink. This will manifest itself in a shrinkage of the whole fibre and the observation of such shrinkage should not be taken to mean that the solvent exchange procedure is inadequate.

The entry of solutes into the microreticular pores is presumably restricted and the water that does enter from a solution may be compared with the 'non-solvent' water of Samuelson *et al.*[32] If electrolytes and polymers cannot pass through these regions, it follows that lignin and hemicellulose must be contained solely within the macroreticular pores: otherwise, pulping processes could not remove them. The implications of this are rather far-reaching, but further speculation is outside the scope of the present paper and will be reserved for a separate publication.

Summary

It has been shown that about 20 per cent of the water in the cell wall of spruce sulphite pulp tracheids exists in pores with a median size of about 35 Å. This size does not change during drying, although the volume of such pores decreases from about 0.16 cm^3/g to less than 0.02 cm^3/g at complete dryness. It is speculated that drying progresses inwards from the exterior of the wall towards the lumen along a sharply defined front and that the pores near the periphery, which close first, tend to remain closed when water is re-added to the fibre. The pores near the lumen, which close towards the end of the drying process, open more readily when water is added.

When pores are closed by drying at 25°C and reopened by water treatment,

the median pore size remains at about 35 Å. Drying at 105°C, however, causes the median size of the pores recovered by water treatment to drop to about 25 Å. This is due to the more permanent closure of the larger pores.

Beating a dried pulp is shown to aid in reopening the pores that closed during drying, but is only completely successful when the conditions of drying have been mild. There is shown to be a qualitative relationship between cell wall porosity and the papermaking properties of a pulp.

An examination of the porosity of fibres that differed markedly in composition and method of preparation revealed that the distribution of pore sizes and the median pore size was the same in all cases. The samples included a regenerated cellulose fibre and the results suggest that the pore size distribution observed with cellulose fibres is not controlled by biological processes. Very little correlation could be observed among the amounts of lignin, hemicellulose or cellulose in the fibre and the permanency of pore closure when the fibre was dried at 105°C and rewetted.

About 80 per cent of the water in the cell wall is not contained within macroreticular pores, but is in a form of molecular association with the cellulose such that its removal by solvents leaves no surface recognisable as such by the nitrogen molecule. The ratio of micro- to macro-reticular pores remained constant during drying so that the study of the latter by nitrogen adsorption should provide information on changes occurring in the system as a whole.

References

1. Page, D. H. and Tydeman, P. A., *Formation and Structure of Paper*, Ed. F. Bolam (Technical Section, B.P. & B.M.A., London, 1962)
2. Statton, W. O., *J. Polymer Sci.*, 1956, **22** (102), 385–397
3. Hermans, P. H., Heikens, D. and Weidinger, A., *J. Polymer Sci.*, 1959, **35** (128), 145–165
4. Stone, J. E. and Scallan, A. M., *Pulp & Paper Mag. Can.*, 1965, **66** (8), T407–T414
5. Clegg, G. C. and Harland, S. C., *J. Textile Inst.*, 1923, **14** T489–T492
6. Yiannos, P. N., *Tappi*, 1964, **47** (8), 468–471
7. Hermans, P. H., *Physics and Chemistry of Cellulose Fibres* (Elsevier Publishing Co. Inc., 1949), 181
8. Barkas, W. W., *The Swelling of Wood under Stress* (H.M.S.O., London, 1949), 11
9. Morton, W. E. and Hearle, J. W. S., *Physical Properties of Textile Fibres* (Butterworth & Co., Ltd., London, 1962), 233
10. Assaf, A. G., Haas, R. H. and Purves, C. B., *J. Am. Chem. Soc.*, 1944, **66** (1), 66–73
11. Rowan, J. W. and Blaine, R. L., *Ind. Eng. Chem.*, 1947, **39** (12), 1659–1663

12. Hunt, C. M., Blaine, R. L. and Rowan, J. W., *J. Res. Nat. Bur. Stand.*, 1949, **43** (6), 547–554
13. Forziati, F. H., Brownell, R. M. and Hunt, C. M., *J. Res. Nat. Bur. Stand.*, 1953, **50** (3), 139–145
14. Haselton, W. R., *Tappi*, 1954, **37** (9), 404–412; 1955, **38** (12), 716–723
15. Merchant, M. V., *Tappi*, 1957, **40** (9), 771–781
16. Thode, E. F., Swanson, J. W. and Becher, J. J., *J. Phys. Chem.*, 1958, **62** (9), 1036–1039
17. Sommers, R. A., *Tappi*, 1963, **46** (9), 562–569
18. Brunauer, S., Emmett, P. H. and Teller, E., *J. Am. Chem. Soc.*, 1938, **60** (2), 309–319
19. Pierce, C., *J. Phys. Chem.*, 1953, **57** (2), 149–152; 1959, **63** (7), 1 076–1 079
20. Roelofsen, P. A., *The Plant Cell Wall* (Gebröder Borntraeger, Berlin Nicolasse, 1959)
21. Emerton, H. W., *Fundamentals of the Beating Process* (British Paper and Board Industry Research Association, Kenley, 1957)
22. Emerton, H. W., *Pulp & Paper Mag. Can.*, 1955, **56** (2), 65–68
23. Washburn, E. W., *Proc. Nat. Acad. Sci. U.S.*, 1921, **7**, 115–116
24. Ries, Jnr., H. E., Van Norstrand, R. A., Johnson, M. F. L. and Bauermeister, H. O., *J. Am. Chem. Soc.*, 1945, **67** (8), 1242–1245
25. Innes, W. B., *Anal. Chem.*, 1957, **29** (7), 1069–1073
26. Robertson, A. A., *Svensk Papperstidn.*, 1963, **66** (12), 477–497
27. Hermans, P. H. and Vermaas, D., *J. Polymer Sci.*, 1946, **1** (3), 149–155
28. Greyson, J. and Levi, A. A., *J. Polymer Sci.*, 1963, **Part A** (1), 3 333–3 342
29. Stone, J. E. and Scallan, A. M., *Pulp & Paper Mag. Can.*, 1965, **66** (8), T440–T445
30. Robertson, A. A., *Pulp & Paper Mag. Can.*, 1964, **65** (3), T161–T168
31. Kun, K. A. and Kunin, R., *Polymer Letters*, 1964, **2** (6), 587–591
32. Grundelius, R. and Samuelson, O., *Svensk Papperstidn.*, 1962, **65** (7), 273–281; Aggebrandt, L. G. and Samuelson, O., *J. app. Polymer Sci.*, 1964, **8** (6), 2 801–2 812
33. Stone, J. E., Aberson, G. M. A. and Scallan, A. M., 1966, to be published

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 areas, because the absorption in this case takes place on the molecules 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 m^2/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.[4] 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^2/g.

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 cross-sections that have appeared in the literature. This is reviewed in reference 4 of the paper.

Discussion

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 thin-walled, 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

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† 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‡ (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

* Vollmer, W., *Chem. Ing. Techn.* 1954, **26** (2), 90–94; Rounsley, R. R., *Amer. Inst. Chem. Eng. J.*, 1961, 7 (2), 308

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

‡ Gc/s = Gigacycle/sec = 10^9 c/s

same linear logarithmic relationship between pressure and concentration or mat density up to mat densities approaching 1 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°F, then sublime it off at −20°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

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 hundredfold. 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

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^2 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.