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THE PATH OF PENETRATION OF PULPING MEDIA INTO WOOD

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IN Giertz' paper, it has been pointed out that the papermaking properties of fibres depend in part on the pulping processes used in their production. The purpose of this contribution is to outline some recent investigations on how morphological factors, especially those that affect the path of penetration of the pulping medium into wood, are of influence on the composition and structure of the fibres ultimately used in sheet formation. The composition of the fibres is especially influenced by the manner of their separation during the pulping process. As background to this discussion, it will be recalled that the basic organisation of a typical fibre or tracheid is as shown in Fig. 1. The layers corresponding to those in Fig. 1 can be seen in the electron micrographs Fig. 2 and 3. Furthermore, as shown by Lange,[1] most of the lignin of the cell wall is concentrated in the region external to the layer S2 and, for *Eucalyptus regnans* and *Pinus radiata* (the species here under discussion), similar values were obtained by Wardrop, Dadswell and Davies.[2] It was shown further in this investigation that the lignin concentration in the middle lamella is greatest at the cell corners and somewhat greater between radial walls than that between tangential walls.

To study the penetration path of liquids into wood, quite simple equipment has been used (Fig. 4). It consisted essentially of providing a means by which liquids could be drawn or forced through the wood in any desired direction at low or elevated temperatures. It should be emphasised that the results obtained using this somewhat artificial system are quite consistent with those obtained when the apparatus was modified to simulate the conditions in a digester; for example, in Fig. 4, the outlet tube could be sealed and the specimen placed in the reservoir *R*. In initial studies, the approach was to stain small blocks of wood using the silver staining method of Coppick and Fowler (1939), the reagents being drawn through the specimen employing the apparatus of Fig. 4. The path of penetration into the wood was established by sectioning material after staining. The influence of pulping media was then

studied by first passing the pulping medium through the specimens for short periods and subsequently staining by the Coppick and Fowler method. From a comparison of the staining pattern in the untreated wood and in that treated with pulping medium before staining, the influence of the pulping medium could be assessed.

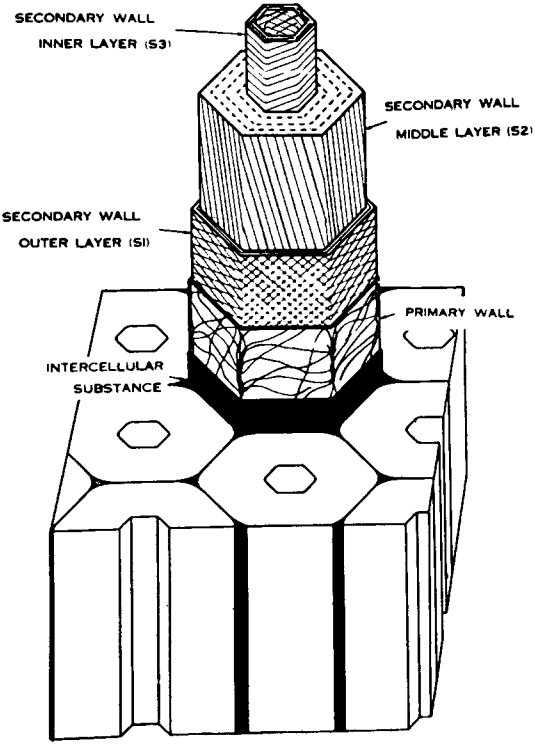


Fig. 1—Diagrammatic representation of the cell wall organisation of a typical wood fibre: note the lamellation of the layers S1 and S3—most of the lignin present lies in the region external to the layer S2

The penetration path and pulping in hardwoods

USING the above methods, it has been shown that for the sapwood of hardwoods the penetrating liquid proceeds first into the vessels from which it passes through the pits to the rays, thence through the pits to the fibres. In heartwood, the initial penetration of the vessels may be retarded in some species by the presence of tyloses. Evidence in support of this path of penetration can be seen in Fig. 5.

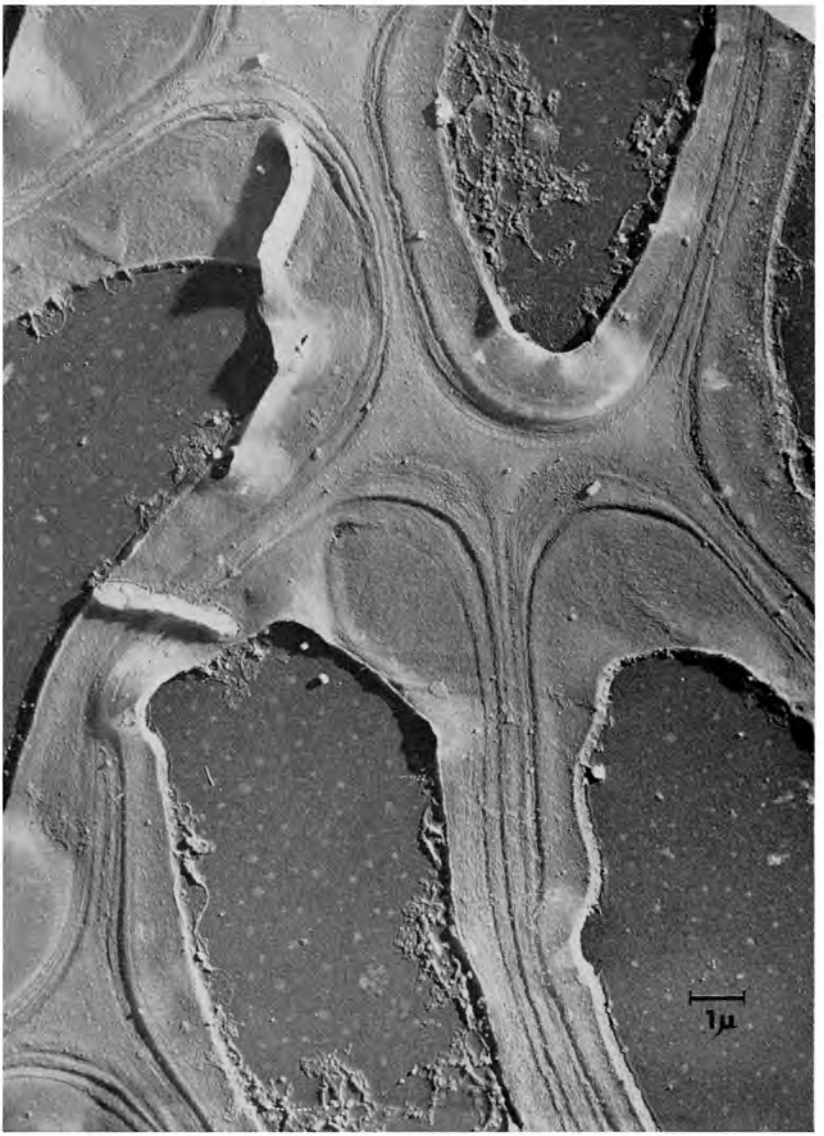


Fig. 2—An electron micrograph of a transverse section of wood from *Eucalyptus regnans*, shadow-cast with platinum-palladium

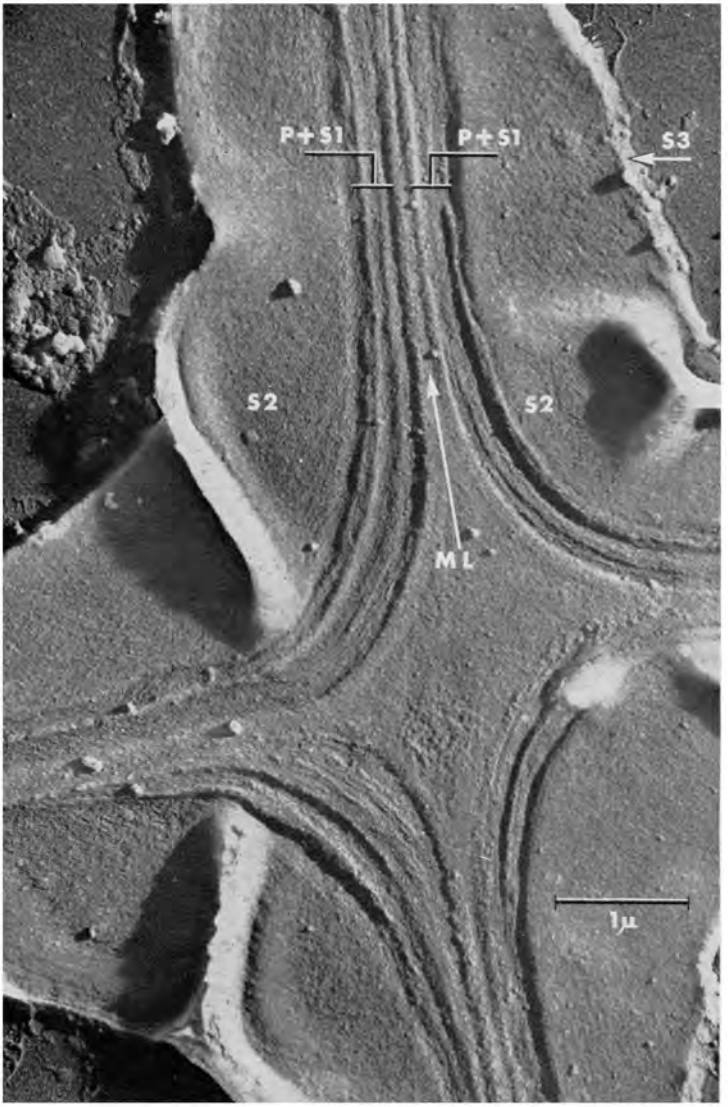
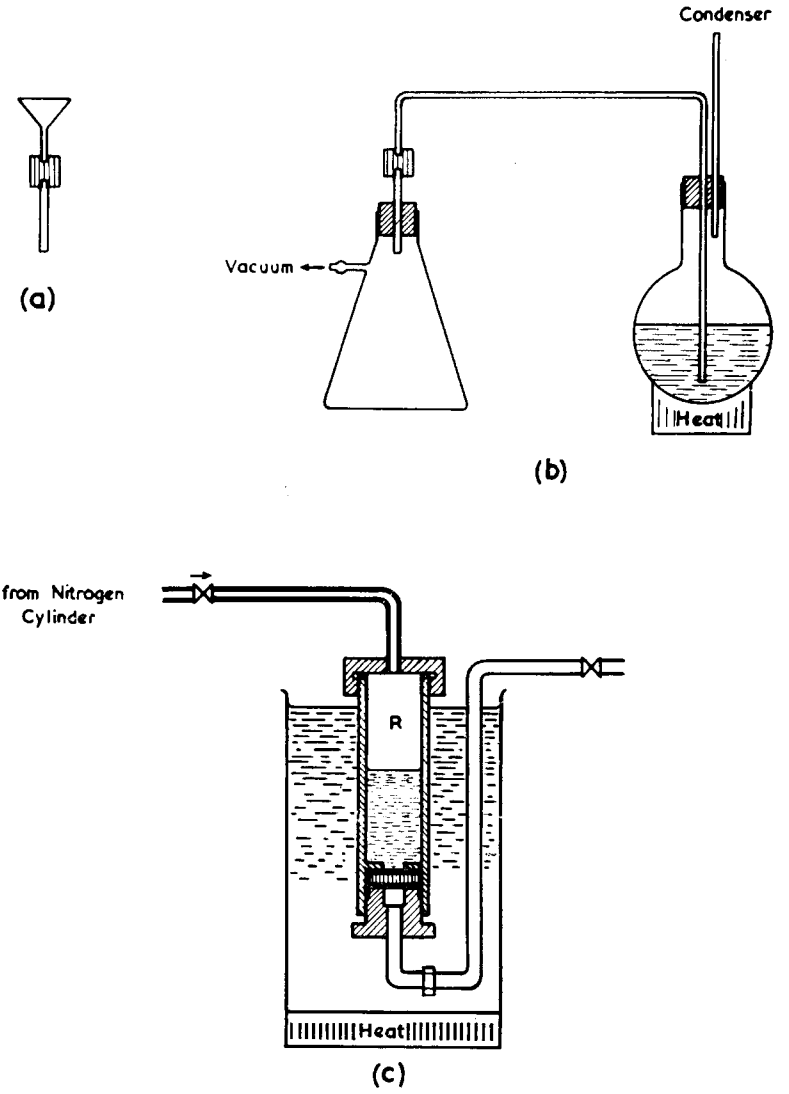


Fig. 3—A similar section to that in Fig. 2, showing details of the various cell wall layers: the primary wall cannot be distinguished with certainty from the layer S1, which is conspicuously lamellated



The apparatus in the lower part of the diagram was used for studies requiring treatment at high temperatures and pressures: in the set of apparatus, the penetrating reagents were drawn through the specimen under vacuum (*a*) and (*b*) or forced through the specimen under pressure (*c*) and the results obtained using this method were comparable with those obtained under conditions assimilating pulping in the digester

Fig. 4—A diagram showing apparatus used in studies of the penetration path of pulping media into wood

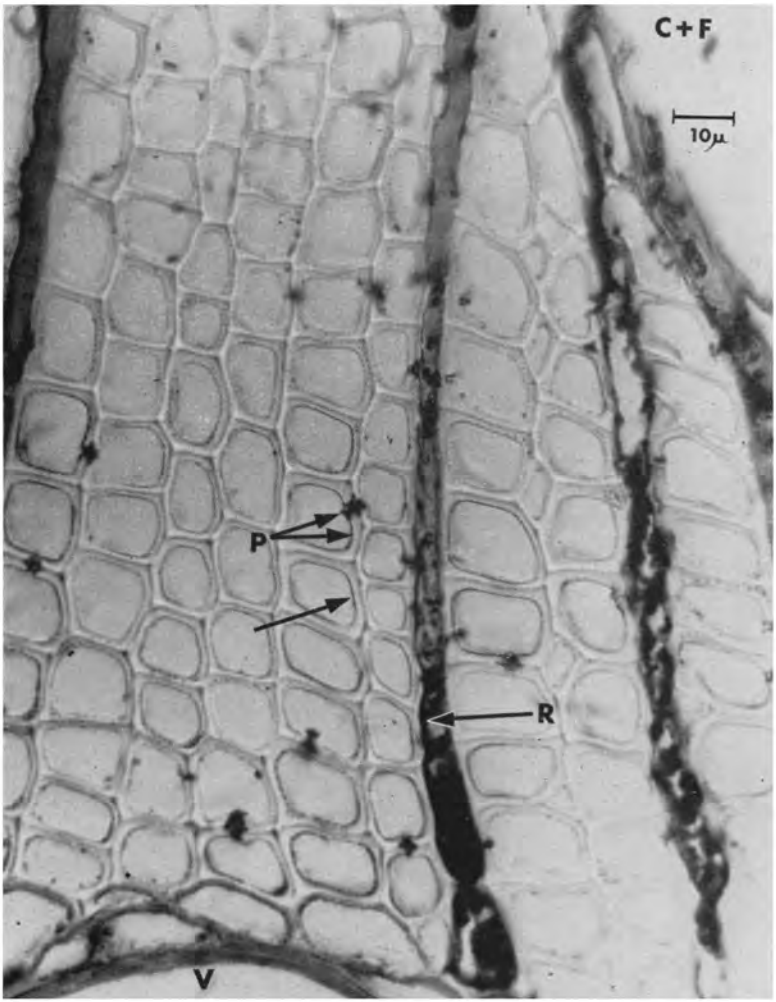


Fig. 5—A transverse section of the sapwood of *E. regnans* cut after treatment of a small block using the staining method of Coppick and Fowler with the apparatus shown in Fig. 4(*a*): note the staining of the wall of the vessel (V) and the extensive penetration of the rays (R) and the staining of the cell wall adjacent to the lumen of the fibres and of the pits between them (P)

The effect of short periods of pretreatment by sulphite cooking liquor at elevated temperatures showed no modification of the penetration path, although the degree of penetration of the wood was enhanced. With hot sodium hydroxide treatment, the degree of penetration of the specimen was increased to a greater degree than with sulphite liquor, but the path, as shown by subsequent staining, was unmodified. There was, however, a remarkably symmetrical zone of penetrated fibres around the penetrated vessels (Fig. 6).

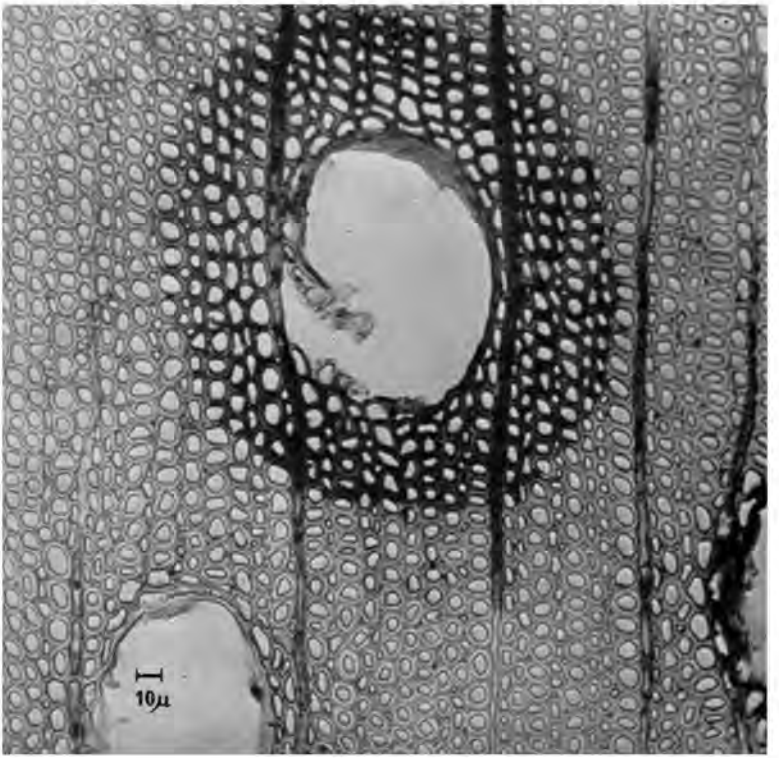


Fig. 6—A transverse section cut from a block treated for 5 min with 6 per cent sodium hydroxide at 100°C and then prepared in the same way as Fig. 5: note the symmetrical movement of reagents away from the penetrated vessel and the advance penetration of the rays; outside the heavily penetrated zone, staining of the cell wall adjacent to the lumen of individual fibres can be seen and of the pits connecting them and it is assumed that these isolated stained fibres were in contact with rays at different levels in the specimen

In an extension of these investigations,[3] the staining method of Coppick and Fowler for studying the lignin distribution has been replaced by ultra-violet microscopy to follow the change in lignin distribution after pulping treatment. This work is still in a preliminary stage, but has yielded results of interest. Sections were cut from untreated specimens (Fig. 7) and from specimens treated with sodium hydroxide (6 per cent at 100°C) for 5 min (Fig. 8)

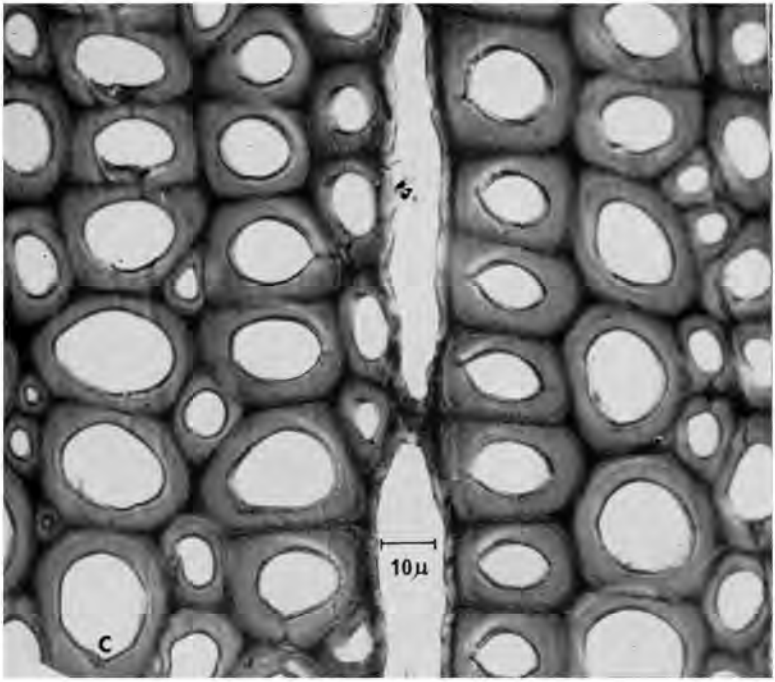


Fig. *7*—An ultra-violet photomicrograph of a transverse section of *E. regnans*

or with neutral sulphite liquor at 100°C (Fig. 9). Comparing these sections, it can be seen that in the S2 region of the secondary wall there are one or more conspicuous zones of absorption. This effect was observed also in ultra-violet photomicrographs of cross-sections of fibres from commercial pulps.[2] It is considered that this change in absorption in the layer S2 arises from adsorption of lignin carried through the specimens by the pulping medium.

It can be seen from Fig. 8 and 9 that even mild treatment results in

some degree of fibre separation. The details of this incipient separation can be seen in the electron micrographs shown in Fig. 10–12 showing sections cut from a block that had been subjected to the treatment with sodium hydroxide. In these, several types of incipient fibre separation can be distin-

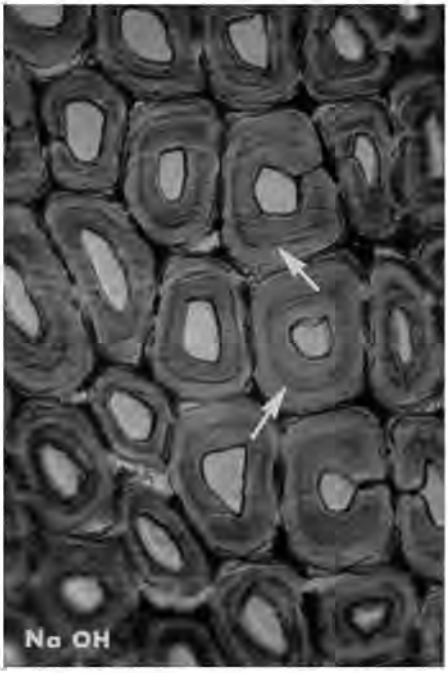


Fig. 8—An ultra-violet photomicrograph of a transverse section cut from a block of *E. regnans* treated for 5 min at 100°C with 6 per cent sodium hydroxide using the apparatus shown in Fig. 4(*b*): note the incipient fibre separation and the zone of increased absorption near the middle of the layer S2 (arrows)—compare with Fig. 7

guished; thus, in Fig. 10, true middle lamella separation is apparent, whereas, in Fig. 11, separation between lamellae of the layer S1 is at a relatively advanced stage and, in Fig. 12, some indication of separation between layers S1 and S2 can be seen.

The different types of fibre separation shown in Fig. 10–12 will obviously

influence the nature of the resultant pulp. Thus, in preparation of pulps involving treatment at high temperatures, middle lamella separation is common, whereas separation with cold soda treatments takes place within the layer S1.[2, 4] The cause of this incipient separation would seem to arise in the stresses set up within the wood as a result of the penetration of the pulping medium.

Fig. 9—An ultra-violet photomicrograph of a section prepared in the same way as Fig. 8, but with neutral sulphite liquor as the penetrating medium—similar features are observable to those in Fig. 8: the zone of absorption in the layer S2 seen in this and the previous figure are also observed in sections of commercial pulps

Penetration path and pulping of softwoods

USING the Coppick and Fowler staining technique, preliminary studies have been made with *Pinus radiata*. It has been shown that initial penetration of the reagent takes place through the open ends of the tracheids and it then proceeds to adjacent cells through the pits. The pits provide the main path

Fig. 10—An electron micrograph of a transverse section of *E. regnans* after treatment with 6 per cent sodium hydroxide for 5 min at 100°C: note the separation in the middle lamella

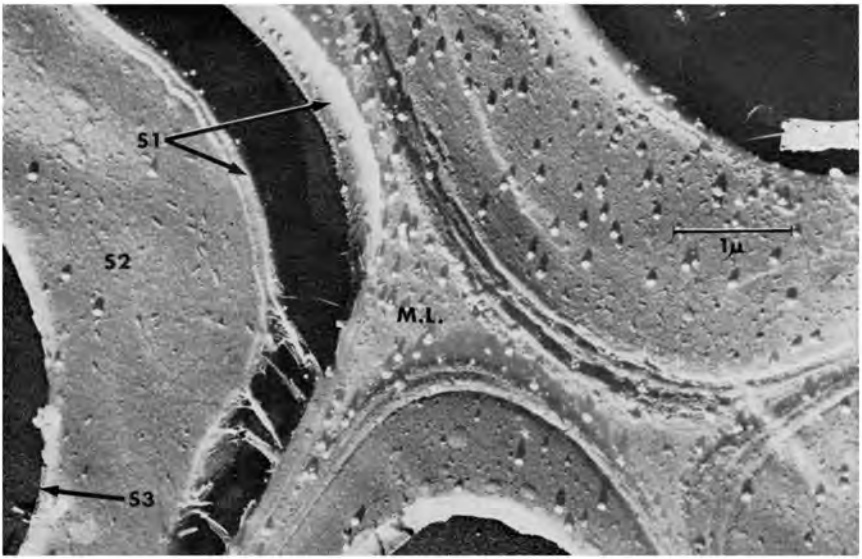


Fig. 11—Similar to Fig. 10, showing separation between lamellae of the layer S1

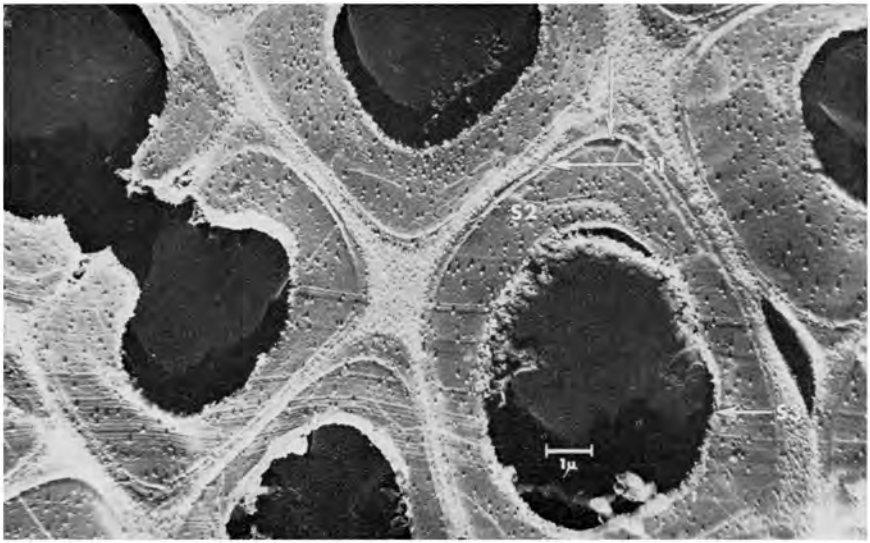


Fig. 12—Similar to Fig. 10 and 11, showing incipent separation between the layers S1 and S2 (arrow)

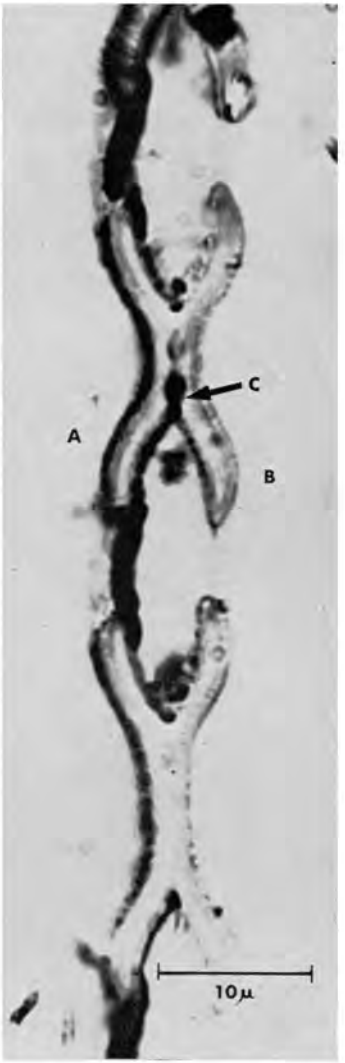


Fig. 13—A tangential-longitudinal section of heartwood of *P. radiata* cut from a block stained by the Coppick and Fowler method, using the apparatus shown in Fig. 4(*c*): note the penetration of the cell *A*, the heavy staining of the torus and penetration of the reagents into the pit chamber (for further description, see text)

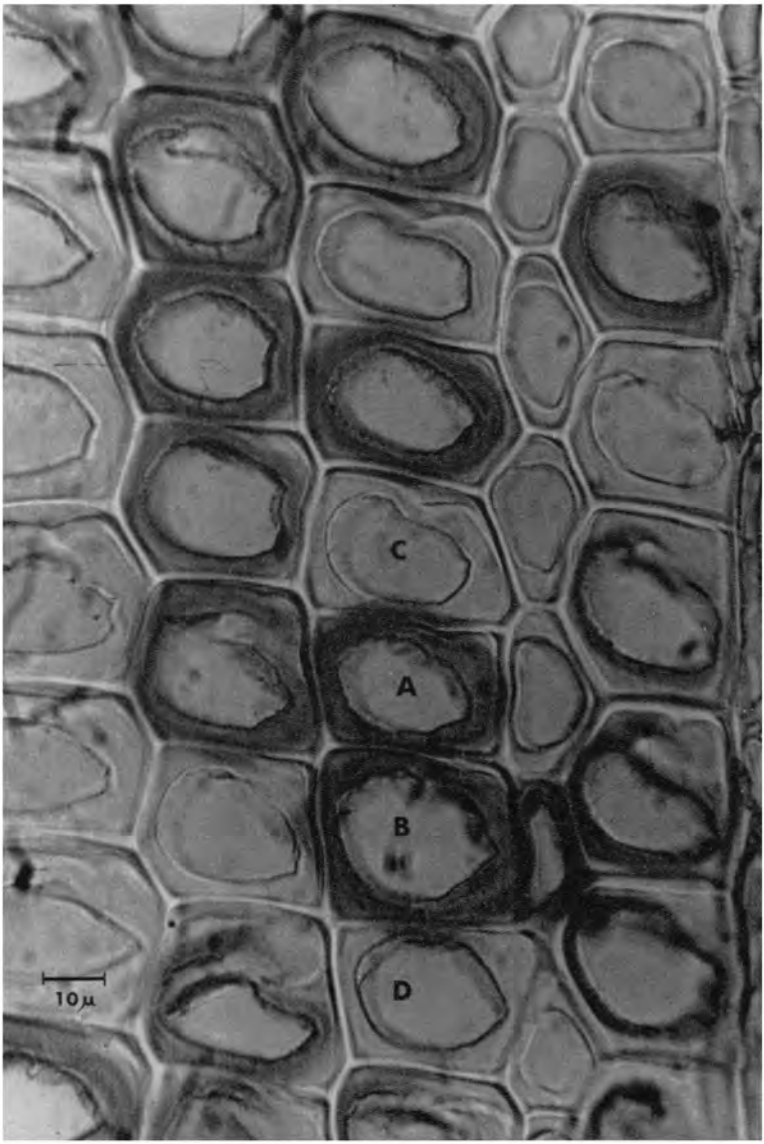


Fig. 14—A transverse section of *P. radiata* cut from a block treated for 5 min at 100°C with 6 per cent sodium hydroxide, using the apparatus shown in Fig. 4(*c*), then stained by the method of Coppick and Fowler: note the symmetrical diffusion from the cells *A* and *B* into the cells *C* and *D* and the unreacted regions near the corners of these cells

of penetration both in heartwood and sapwood, apparent even when marked aspiration of the pits had occurred. Penetration of the liquid, as shown by the straining reactions, indicated the passage from the lumen of one cell through the pit to that of an adjacent cell.

Thus, in Fig. 13, two adjacent tracheids of heartwood are shown in which the pits are aspirated and it is apparent that penetration of the staining reagents had taken place into the cell *A* and extended through the pit chambers

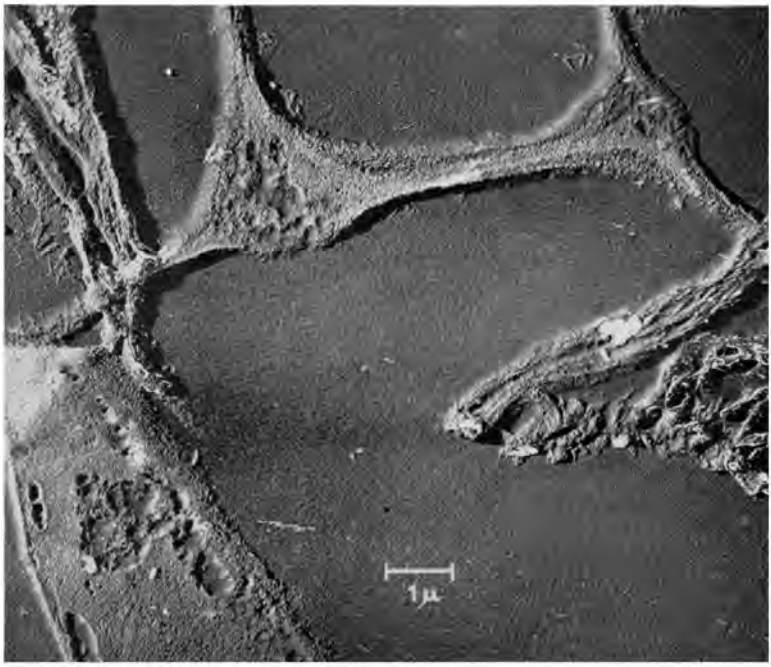


Fig. 15—An electron micrograph of a section from a commercial sulphite pulp, showing the presence of unreacted corner thickenings

towards the cell *B*, but had not reached cell *B*. It may be noted that, in general, the staining reagents did not penetrate the middle lamella from the pit chamber as proposed by Lange.[5] The only evidence of this was at point *C*.

The failure of the staining reagents to penetrate into the middle lamella appears to be related to the relatively less permeable nature of the middle lamella and of primary wall compared with the layer S1, also to the structure of the bordered pit.[3, 6]

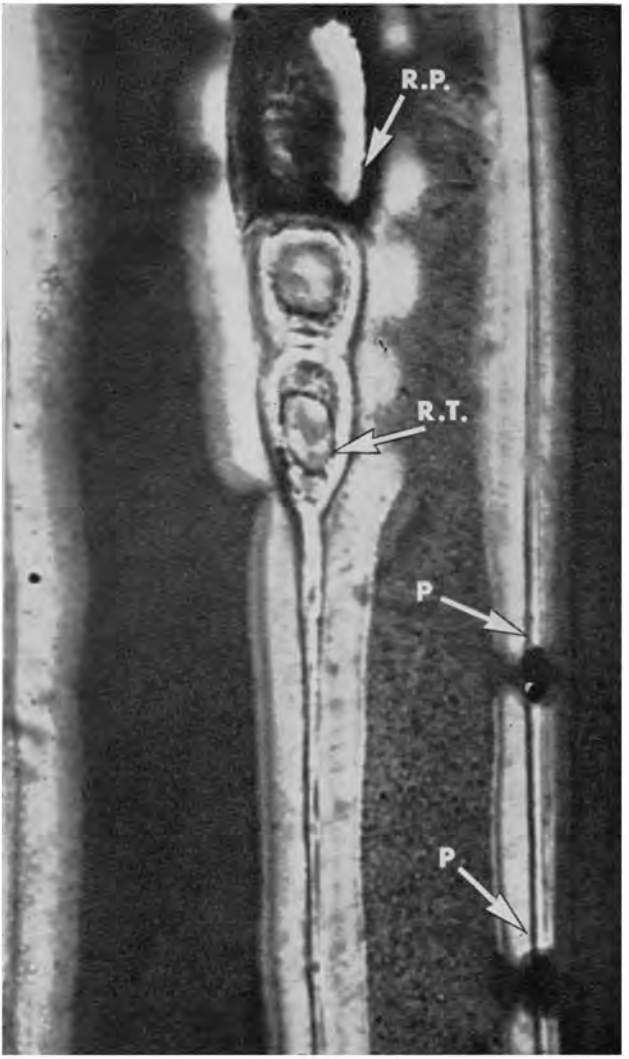


Fig. 16—A tangenital-longitudinal section of *P. radiata* cut from a block that was stained using the method of Coppick and Fowler in the apparatus shown in Fig. 4(*c*), for which the specimen was prepared so that the reagents were forced radially through it: note the heavy penetration of the ray parenchyma (RP) and the relatively slight penetration of the ray tracheids (RT); the wall adjacent the lumen of the tracheids was heavily stained, but there was little staining of the remainder of the cell wall, except where the reagents had passed selectively through the pits (P)

After mild treatment with pulping media, the path of penetration was not changed. After the medium reached the lumen of the tracheid, diffusion then appeared to take place through the cell wall. The direction of diffusion did not appear to be influenced by the wall layers through which the medium passed. This can be seen in Fig. 14. The tracheids *A* and *B* were penetrated, but the tracheids *C* and *D* were not. It can be seen that the medium had diffused from the tracheids *A* and *B* into the cells *C* and *D*, but the direction of diffusion was quite symmetrical.

From this, it is apparent that the last region of the cell wall to react with the penetrating medium was the middle lamella and especially the middle lamella at the cell corners, where in fact the lignin is at its highest concentration. In view of this pattern of penetration, it is not surprising that in lightly cooked pulps the unreacted corner thickenings can often be detected (Fig. 15).

Some lateral penetration takes place through the ray cells and it appears that penetration proceeds more easily through the ray parenchyma than through the ray tracheids (Fig. 16). The above investigations are at present being extended with special reference to the study of semi-chemical pulping processes and to preservation treatments. It will be apparent, however, with the path of penetration that has been demonstrated in mind, that a pulping medium will be longest in contact with the relatively unlignified inner layers S2 and S3 of the secondary wall and will be contact for the shortest time with the lightly lignified middle lamella. Because of this, it can be understood that considerable degradation of the cellulose will take place during the cooking process.

REFERENCES

1. Lange, P. W., *Svensk Papperstidn.*, 1950, **53** (23), 749–766
2. Wardrop, A. B., Dadswell, H. E. and Davies, G. W., *Appita*, 1961, **14** (6), 185–202
3. Wardrop, A. B. and Davies, G. W., *unpublished* (1961)
4. Wardrop, A. B. and Dadswell, H. E., *J. Inst. Wood Sci.*, 1958, (2), 8–21
5. Lange, P. W., *Svensk Papperstidn.*, 1947, **50** (11B), 130–134
6. Wardrop, A. B. and Davies, G. W., *Holzforsch.*, 1961, **15** (5), 129–141

DISCUSSION

MR. P. E. WRIST: One statement made during the presentation of this paper was of great interest to me—that beating has the effect of stiffening a fibre. I think this is an important statement and worthy of more discussion.

It is often stated in the literature that one of the effects of beating is to make the fibre more flexible. In our studies of fibre networks in suspensions, however, we have always had difficulty in explaining why the network strength of a beaten pulp was lower than that of the unbeaten pulp. The two effects of fibrillation and of increased fibre flexibility (which are usually attributed to beating) should both have made the flocs stronger and the only factor by which we could explain this weakening of the floc structure was the shortening of the fibres. Having measured fibre lengths, we found that in the cases we studied we had not shortened the fibres very much. An enormous dependence of strength on fibre length would therefore offset the other two effects. If we can accept, however, that beating stiffens the fibres in suspension, then our experimental data can be explained more reasonably.

The distinction you have made between increased stiffness in the wet swollen stage and increased flexibility during the drying phase is not adequately appreciated in the literature.

DR. O. J. KALLMES: With regard to discussions on the flexibility of fibres, we must keep in mind the axis of reference of the fibre's cross-section. Fibres that have undergone mechanical treatment tend increasingly to collapse, making them more flexible around their y axis, but less around their z axis. The former effect enhances the bonding ability of fibres, the latter makes them more rigid within the sheet when the sheet is strained.

PROF. G. JAYME: Giertz has pointed out the difficulties of removing lignin from plant materials without removing hemicelluloses. There are two approaches. Maass showed about 30 years ago that a sulphite cook of wood at 50°C will yield a pulp that may be regarded as a holocellulose containing practically all of the hemicelluloses originally present. Another way has recently been used by us—a cold soda pulp was prepared from poplar wood at about 93 per cent, which could be delignified easily with sodium chlorite practically without removal of hemicelluloses. These could be removed by treatment with caustic soda solutions of various concentrations. The strength data on the pulp prepared in this way indicated that strength increased very

considerably with lignin removal, whereas the influence of the hemicelluloses was less pronounced. The highest strength data were obtained when all the lignin and part of the hemicelluloses were removed.

DR. G. N. RICHARDS: To what extent is fibrillation affected by hemicelluloses alone? For instance, what is the fibrillation behaviour of a holocellulose in which only the lignin has been removed and all the hemicelluloses remain? —are the fibrils held together by a hemicellulose glue?

PROF. H. W. GIERTZ: It is quite possible to fibrillate holocellulose fibres, but, because of the slippery consistency, it must be done in the right machine. The Lampén ball mill, for instance, is unsuitable.

DR. S. G. MASON: Giertz has stated that lignin is hydrophobic. In view of the fact that water is sorbed by lignin (as shown by our own work and that of Christensen in Australia) and that water acts as a plasticiser for lignin, I find this concept doubtful. What is the experimental evidence for this claim?

PROF. GIERTZ: For small molecules, the terms *hydrophilic* and *hydrophobic* are well-defined. A problem occurs when dealing with large molecules and macro-molecules. Propanol, glycerol and phenol are hydrophilic and anisole (methoxybenzene) is hydrophobic—but what about lignin? Many substances are neither typically hydrophilic nor typically hydrophobic, they are something in-between and may be graded in this respect over a very wide spectrum.

From a practical point of view, the words should in each case be used appropriate to the conditions concerned. Let me take an example. Secondary cellulose acetate with a D.S. of 2·0–2·5 is less hydrophilic than cotton and viscose rayon are, because it absorbs less moisture and is plasticised less in laundry operations. As a textile, secondary cellulose acetate belongs to the hydrophobic filaments. This is still truer for cellulose acetate with a D.S. of 2·8–2·9. On the other hand, a cellulose acetate film with a D.S. of 2·9 is considered to be hydrophilic when used as a loudspeaker membrane, because it becomes slightly plasticised by the moisture in the air. For this purpose, it has to be a true triacetate.

Hemicellulose is hydrophilic, but a sol of cellulose micelles, prepared by hydrolytic degradation of wood cellulose is classed by Rånby as hydrophobic, despite the fact that the precipitated sol material absorbs moisture. There is such an important difference in behaviour towards water between a groundwood fibre and a holocellulose fibre or between precipitated gamma-cellulose and precipitated alkali lignin that to my mind this difference is expressed most simply and accurately by using the words hydrophilic and hydrophobic.

MR. J. W. SARGENT: I should like some comment on the fact that patterns of microfibrils similar to those Giertz has visualised for the S2 cell wall layer are to be found in such two completely different fibres as bleached sulphite and unbleached kraft.

PROF. B. G. RÅNBY: It is not a question of the strength of the individual hydrogen bonds and we know that the hydrogen bond energies are between 3 and 10 kcal/mol. Under certain conditions, you can form many ordered hydrogen bonds (as in crystalline regions), in ordered adsorption of hemicellulose chains on to cellulose microfibrils or in ordered aggregation (association) of a bundle of cellulose microfibrils. The resistance of such systems, say, to swelling with water is because the swelling reagent must give a simultaneous opening of a whole sequence of identical bonds and this is thermodynamically unfavourable, because it is unlikely. The insolubility of cellulose in water can be interpreted along these lines.

PROF. JAYME: The influence of hemicelluloses on light scattering in handsheets is very marked. Jayme and Pommer proved many years ago, using the Kubelka–Munk method and formula, that the scattering coefficient of handsheets closely followed the alpha-cellulose content changes obtained by the caustic soda treatment of pulps—with progressive removal of hemicelluloses, the handsheets became more opaque.