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THE REARRANGEMENT OF MICROFIBRILS IN DRIED CELLULOSE AND THE IMPLICATION OF THIS STRUCTURE ALTERATION ON PULP PROPERTIES

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If we look at an electron micrograph like Fig. 1 representing a thin cellulose membrane hanging from a fibre that has been dried, we may at first suppose that this picture represents an artefact formed during the preparation or within the electron microscope. Pictures similar to this one found by Stemsrud on the membranes of bordered pits in pine wood were interpreted by him as natural perforations developing in pit membranes of older tracheids. We also had found perforated membranes in pine wood and we published our view in 1955, according to which this perforation is due to drying effects on cellulose. In autumn 1956, Frey-Wyssling, Mühlethaler and Moor described (in *Mikroskopie*) these perforations on thin cellulose membranes as being artefacts formed due to the heat of the metal and carbon-shadowing procedure in the vacuum chamber.

These perforations on thin cellulose membranes were only observed with the application of the carbon replica method developed by König and later transformed by Bradley to a high vacuum carbon evaporating method. These methods only were able to show thin lamellas, which disappeared when applying formvar, collodion or polystyrene replicas. Only the carbon method depicts a hole in the object as a hole also in the replica, whereas the holes are filled out with the replica substance with the other methods.

The wood fibre transformed into pulp has lost most of its lignin and a large amount of its hemicelluloses and other substances either amorphous or of short chain length. The fibre begins to shrink, to twist and to collapse when being dried, which was observed and described by Emerton. The well-known reason of this effect is the formation of hydrogen bonds between neighbouring microfibrils, which bring these fibrils into closer contact and thus, by eliminating the interfibrillar spaces, the whole fibre has to shrink. It is difficult to prove occurrence of a microfibril rearrangement within the different fibre walls. When studying differences between sulphite and sulphate pulps, however, we found that the pictures taken of the two pulps beaten to a corresponding freeness (°S.R.) differed considerably as shown in Fig. 2 and 3. Fig. 2 represents a sulphite pulp beaten to 58° S.R. We recognise a loose mass of microfibrils, more or less present as single individuals. On the other hand, Fig. 3 shows a sulphate pulp of 59° S.R. that took more than twice the time to reach this degree of beating and we find many small microfibril strings or rods, which were at first glued together and later on were broken down mechanically by the beating treatment. The sulphite process topochemical in action had affected the deeper located walls very little. The native state of the microfibrils and their accessory substances had been untouched and they easily separated during the beating treatment from one another reaching the same degree of hydration much earlier than the sulphate pulp. This pulp had to be broken down to such small units of microfibrils in order to reach the same degree of beating and yet, as the pictures show, the general state of the two pulps is wholly different. The higher internal microfibril contact of the sulphate pulp results in a lower water retention value. The pulp is more highly hornified than is the sulphate pulp. The drying effects on cellulose structures become evident as an aggregation of microfibrils into small bundles, strings or rods. It should therefore also be possible to detect them on thin freely hanging cellulose lamellas. It is obvious, furthermore, that the formation of microfibril strings must result in holes appearing at the places of the dislocated microfibrils, since the lamella as a whole is not able to shrink as a unit.

In cell walls, we distinguish the two dominant microfibril arrangements of interwoven structures in the primary walls (Fig. 4) and a parallel structure in the secondary wall (Fig. 5). If we assume now that the microfibrils will be brought into closer contact during drying, thin lamellas of microfibrils, which are partly hanging free, will then dry in the following manner. Parallel-lying fibrils (Fig. 6) will approach each other most in the middle of the bundle, where their ability to move is greatest. The bordering fibrils are

stretched the most and, if their elongation ability has come to an end, an oval hole will form in the lamella. We have dried a microfibril suspension of sulphate spruce pulp on perforated formvar membranes and then palladium-shadowed it. We find this gives pictures very similar to the schematic drawing (Fig. 7). Interwoven structures on the other hand will be able to aggregate only to very short microfibril bundles, since the participating microfibrils will aggregate with neighbouring fibrils running in other directions. Thus, theoretically the position shown in Fig. 8 will result, if the net is strictly rectangularly formed and if the distance between the wet fibrils does not change; in any case, we will find more or less round pores in dried interwoven microfibril sheets. Besides, the suspension dried on formvar supports shows corresponding results (Fig. 9).

The membranes of bordered pits of softwood are fastened to the pit chamber at their periphery and dry over the pit aperture of a non-collapsed fibre as a free-hanging lamella. Once more, we find the same picture as with the structures dried experimentally (Fig. 10). We even can follow each individual microfibril as it combines with its neighbour until the elongation resistance does not allow further unification in this direction and the one fibril quickly unites with another.

In order to exclude the effect of the heat in the shadowing chamber, we examined the suspension described above directly in the electron microscope without metal shadowing and obtained the same picture again (Fig. 11). These results confirmed our opinion that these ring-net structures are caused by the drying forces and we now re-examined polystyrene replica images.

We took a radial cut of pine wood, which we delignified for 1 hr. with sodium chlorite. Then we took a vacuum replica with polystyrene, destroyed the object in sulphuric acid and shadowed the replica only, thus being absolutely certain to obtain a picture of cellulose structures influenced by drying effects only and not damaged either in the vacuum chamber or in the electron microscope. Once again, the same structures were observed (Fig. 12), this picture being one out of many similar pictures taken (looking out of the cell cavity against the closing pit membrane).

We had already been able to show on electron micrographs how thin cellulose lamellae, which are hanging from a fibre after the chemical and mechanical treatment of the pulping process, form the fibre-to-fibre bondings in paper and pulp sheets. The lamellae dry on to the neighbouring fibre by hydrogen bonds and thus link the two fibres together. One of these pictures is shown in Fig. 13. Here, we can clearly study the nature of the drying

process. The torn part of the primary wall of the upper fibre has come into contact with the lower one. When the water was removed, the microfibrils dried together laterally and downwards. The fibrils at the edges again experienced the greatest dislocation and thus the highest strain. They free themselves therefore from the support much earlier than do the middle microfibrils. Along the parabola-shaped boundary of the lamella, between what has dried into intimate contact with the fibre and what is freely suspended, the same drying strain acts on each microfibril that is detached from the substratum. The freely hanging part, being unable to shrink further, perforated again in the manner described above. Attention may be paid to the shadows of the pores to be seen underneath the perforated lamella, which could hardly be thrown so distinctly, if the disarrangement of the lamella were to take place only at the very moment of metal shadowing.

This is why the picture shown first and many other pictures seen in the electron microscope raise such suspicion in the observer's mind that an artefact is being observed. If we look at Fig. 14, we again recognise two fibre-to-fibre bondings having a very unnatural aspect, for the following reason. The microfibrils, drying together, lost their interfibrillar space and in places so nearly approached each other that the resolving power of the applied shadowing technique no longer sufficed to distinguish individual fibrils. In addition to this, the structure was rendered indistinct by the carbon, which not only covered the surface, but by its diffuse scattering surrounded the microfibrils on all sides. The electron beam thus had to penetrate two carbon layers, which resulted in a corresponding scattering of electrons and these regions consequently appear darker than does the surrounding area. The fibrillar structure was coated with a carbon coating, an effect shown in Fig. 15. We tried therefore to replicate a fibre surface in the following way. We shadowed the object with palladium, backed it with polystyrene, destroyed the cellulose, cleaned the polystyrene/palladium layer with a jet of water, dried and shadowed them with carbon. The carbon thus formed the support for only a thin palladium layer, which represented in fact the top surface of the object. Fig. 16 shows the net formed by the microfibrils having dried together in this state and Fig. 17 shows another fibre-to-fibre bonding that has lost this artefact-like appearance.

We may conclude that, according to our results, the perforation of thin cellulose lamellae is due to drying effects on the cellulose occurring even at ordinary temperatures, which bring the microfibrils into closer contact and which, on thin, partly free-hanging lamellae, result in a lateral dislocation of the microfibrils, thus opening spaces between them. These spaces are

formed according to the microfibril arrangement prevailing in the wet lamella, they appear as oval pores in the case of parallel oriented structures and round pores in the case of interwoven microfibril structures.

A strange appearance sometimes to be seen in these structures can be attributed to the close arrangement of the dried microfibrils and to the smearing and coating effect of the metal and, in particular, of the carbon shadowing.

These structures show the ready tendency of microfibrils to aggregate in the case of being chemically deprived of their natural protecting substances. A pulp once dried will therefore show a remarkable loss in water retention value, its ability of forming a sheet will be considerably reduced by the hornification effects of the first drying. These effects may only partly be overcome by beating and the formation of new contacting lamellae. Therefore, the loss of strength caused by drying a pulp remains irreversible to a large extent.

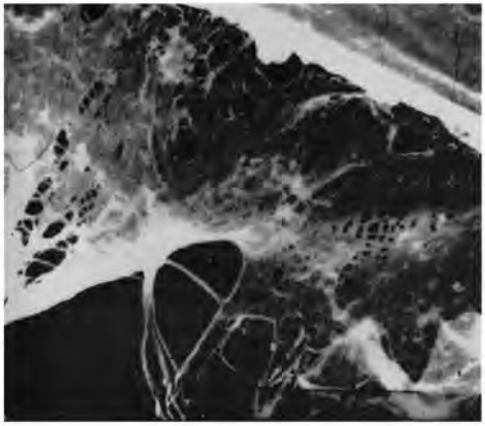


Fig. 1

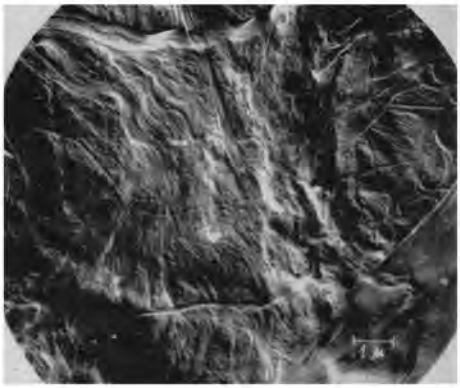


Fig. 2

Fig. 3

Fig. 4

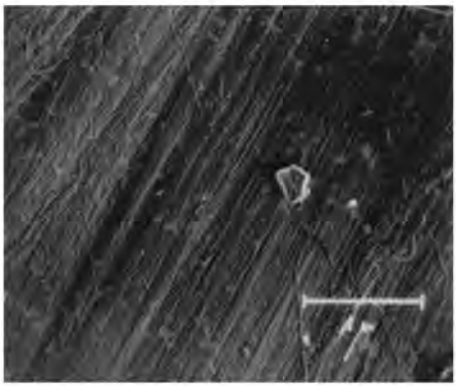
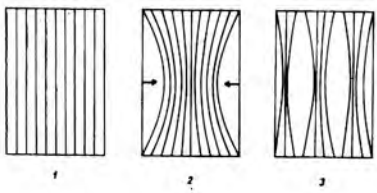


Fig. 5



Drying structures in parallel microfibrils.

Fig. 6

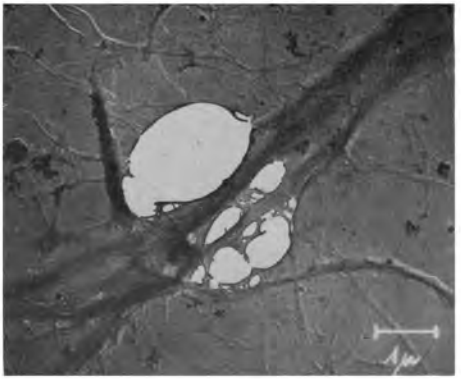
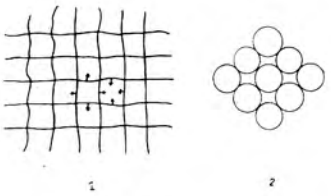


Fig. 7



Drying structures in interwoven parallel microfibrils.

Fig. 8

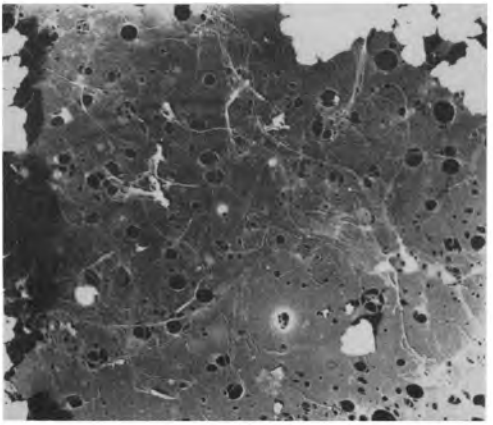


Fig. 9

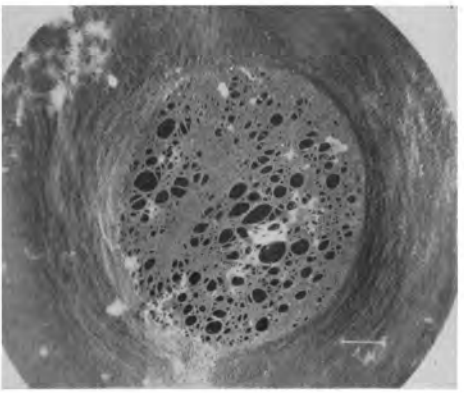


Fig. 10

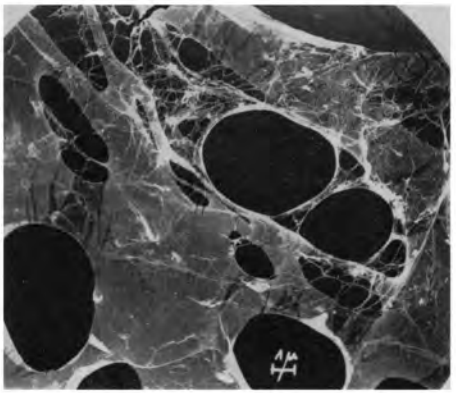


Fig. 11

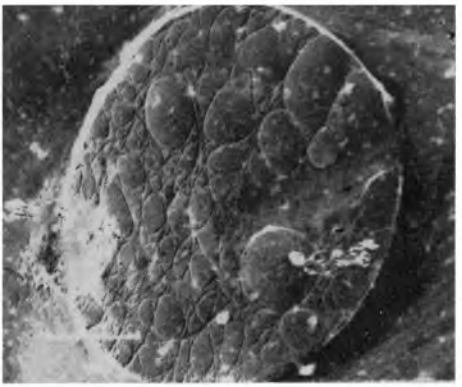


Fig. 12

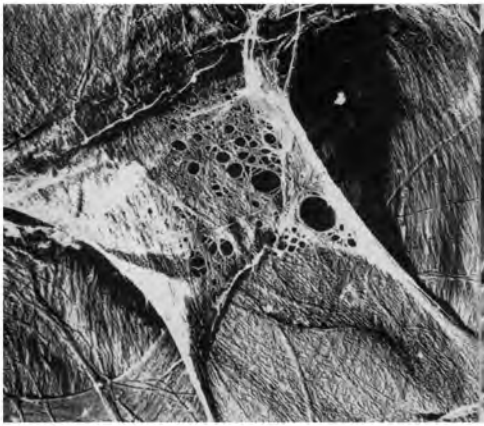


Fig. 13

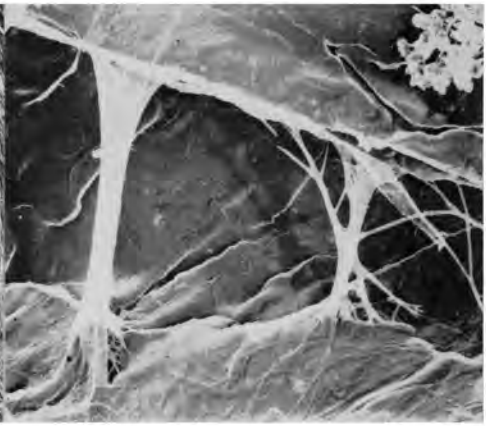


Fig. 14

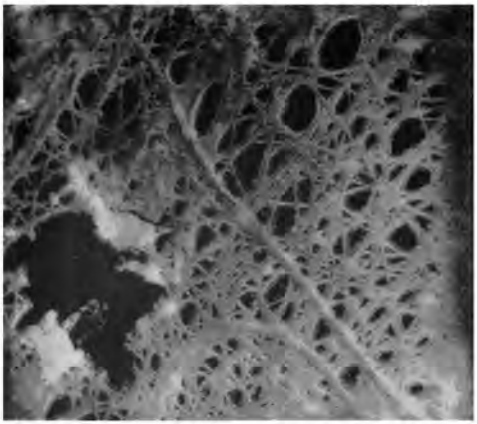


Fig. 15

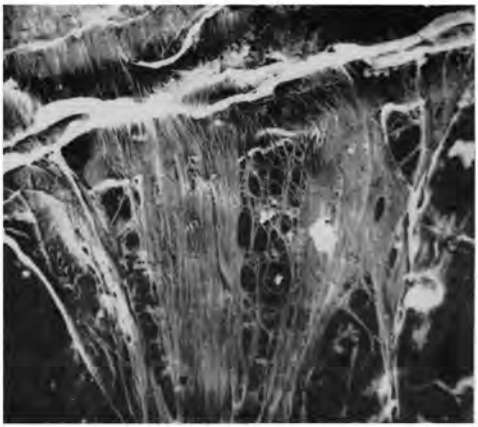


Fig. 16

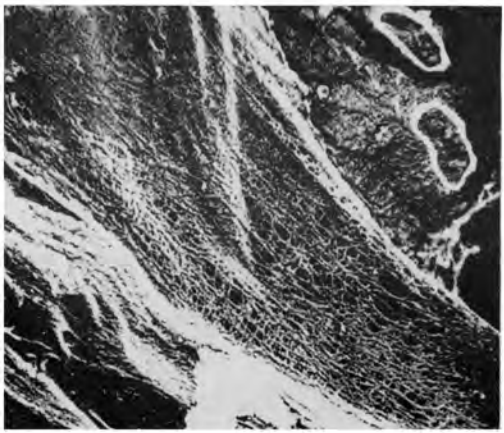


Fig. 17

DISCUSSION

CHAIRMAN: I would like to give an opportunity now for the discussion of any details of Mr. Hunger's paper, in advance of Session 3.

MR. P. E. WRIST: In the light of your subsequent argument about the difference of drying down the parallel fibrils and the reticular fibrils, Mr. Hunger, to what factors do you attribute the difference between the sulphite and sulphate pulp micrographs that you showed very early on in your contribution?

MR. HUNGER: We found that the sulphite process only proceeds topochemically, thus leaving the deeper walls untouched in their later state, so that the microfibrils are more or less still surrounded with their protective substances such as hemicellulose and lignin. In the sulphate fibre, however, after the cellulose is destroyed, the lignin is found as an amorphous mass, contrary to the sulphite fibre, when it still remains in the form of the fibre. This sulphate fibre is swollen to such an extent that all its amorphous layers have been destroyed. Though still there, they are more or less statistically distributed over the fibre and, to a certain extent, no longer in their native places; these fibres are thus usually able to dry together in high hornification.

MR. A. P. TAYLOR: Might we have an idea of the approximate range of magnification in the slides we have just seen?

MR. HUNGER: The dot shown is one micron. The magnification you saw, with the enlargement of the projector, would have been 100 000 — 300 000.