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ELECTRON MICROSCOPE 2- AND 3-DIMENSIONAL CLASSIFICATION OF FIBRE BONDING

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Synopsis

Using a technique developed by the authors, an examination by electron microscopy of coniferous wood tracheids has shown that the secondary alterations in the texture of the cell wall layers during drying play an important role in fibre-to-fibre bonding. Differences between late wood and early wood are indicated, together with the typical behaviour of each of the cell wall layers in such bonding. The effects of beating, of drying a sheet of paper and reforming it from the disintegrated pulp are dealt with, particularly regarding their influence on sheet strength.

La classification en deux et trois dimensions des liaisons entre fibres au moyen du microscope électronique

Les auteurs ont étudiée, par une technique qu'ils ont mis au point, les trachéides de conifer. D'après leur examen il ressort que les modifications secondaires de la texture des couches de la paroi cellulaire survivent en cours du séchage jouent un rôle important dans les liaisons entre fibres. Les auteurs mentionnent les différences observées entre le bois d'automne et de printemps ainsi que le comportement spécifique dans de telles liaisons de chaque couche.

Ils traitent des effets de l'engraissement et du séchage d'une feuille et de sa reconstitution après désintégration en insistant sur l'influence de ces traitements sur la résistance de la feuille.

Zwei- und dreidimensionale Klassifizierung von Zwischenfaserbindungen mit Hilfe des Elektronenmikroskops

Mit einem von den Autoren entwickelten Verfahren konnte durch das Elektronenmikroskop bei Nadelholztracheiden aufgezeigt werden, dass die sekundären Veränderungen im Aufbau der Zellwandschichten während der Trocknung eine wichtige Rolle für die Zwischenfaserbindungen spielen. Es wurden sowohl die Unterschiede zwischen Spät- und Frühholz als auch das typische Verhalten jeder einzelnen Zellwandschicht bei der Bildung derartiger Bindungen dargestellt, ebenso wie die Auswirkung der Mahlung, der Trocknung und der Blattbildung aus aufgelöstem Stoff- besonders im Hinblick auf die Blattfestigkeit.

Introductory remarks

THE mechanism of fibre bonding has for a long time been the subject of many investigations. Starting with the findings of Strachan,[1] Urquhart[2] and Campbell,[3] a new phase started in research directed to fibre-to-fibre bonding. With the support of infra-red spectroscopy, X-ray investigations and electron microscopy, one arrived at the conception now generally accepted that the bonding within the pulp fibres and the paper formed from them rests to a very large extent on hydrogen bonds that become active between OH groups, if their oxygen atoms approach each other to a distance of less than 2.5 Å.

The electron microscope was the first instrument by which the finest fibre-to-fibre bonds could be made visible to the human eye. Contributions in this field, however, have remained rather scarce,[4-9,15,38,50-52,63] owing to the fact that for a long time the showing of bonds represented an apparently unsurmountable difficulty. The transmission electron microscope is only able to radiate through layers of extreme thinness not exceeding a few hundred Ångström units; therefore, the direct investigations of fibres and fibre bonds by this method remained impossible and other types of electron microscope were used. In England, the research team of Emerton, Page, Watts and Amboss[4,5,6,10] at the institute in Kenley resorted to the reflection electron microscope, whereas Smith[11] at the Pulp and Paper Research Institute in Montreal recently applied a scanning electron microscope with a technique considerably improved by himself. Both types offer the advantage that the object is examined directly by imaging the electrons scattered from the surface, thus eliminating the thickness of the object as an influencing factor. They also supply pictures giving a certain plastic impression, though these are

unfortunately not dimensionally true and, moreover, the resolving power of these methods at the present time is about one power less than that obtainable by means of transmission procedure.

It was the aim of the research team in England therefore to find a method of observing surfaces of pulp fibres and papers in transmission microscopy and a suitable method was developed by Page.[12,13] It represents a replica method, which reveals quite well the rough surface of pulp fibres as such, but fails to show the very thin lamellae as elements of fibre bonding.

It meant considerable progress when Comer, Statson and Lyons[14] in U.S.A. and simultaneously Jayme and Hunger[15] in Germany developed a *direct replica method*; the pulp or paper surface is directly treated with metal vapour (Williams and Wyckoff[16]), the metal film obtained shadowed by a thin carbon film according to Bradley[17]; then the double layered film is supported by means of polystyrene and the cellulose destroyed, thus leaving a replica that yields excellent electron micrographs.

For supporting the metal/carbon film, a vacuum method developed earlier by Hunger and Jayme[18] was applied that enhanced the reproduction of very fine details. We take this opportunity to emphasise that this method was developed and used by us completely independently from Comer[19] *et al.* and that we certainly did not 'modify' the Comer method as assumed by Page and Emerton.[20] By means of this direct replica preparation method, we could now reproduce quite exactly such very rough surfaces as of sheets from unbeaten pulps and show for the first time fibre-to-fibre bonds of a thickness of only a few hundred Ångström units and reaching through the space between the fibres.

Texture of tracheids

It is considered necessary for the understanding of the various electron micrographs shown to refer again to the texture of the different cell wall layers composing the total cell wall and thus of the tracheid.

Fig. 1 shows the model of a pine tracheid. Into the smooth middle lamella (ML), consisting chiefly of lignin and some pectic substances, the primary wall (P) is embedded, consisting of more or less randomly oriented and loosely interwoven microfibrils. The next layer is the outer secondary wall (S1), consisting of at least two layers of microfibrils crossing each other end and of an average direction corresponding to a helical orientation almost perpendicular to the fibre axis. Then follows the inner secondary wall (S2), which according to Jayme and Fengel,[20] represents about 78 per cent of the cross-section of the wall of an early wood spruce tracheid; this thickest layer of all consists of microfibrils oriented practically parallel

to each other and winding around the fibre axis at a very small angle to the axis. Finally, the total cell wall is closed to the lumen by a very fine inner secondary wall (S3), often also termed the tertiary wall, the texture of which is very similar in the case of conifer tracheids to that of the layer S1.

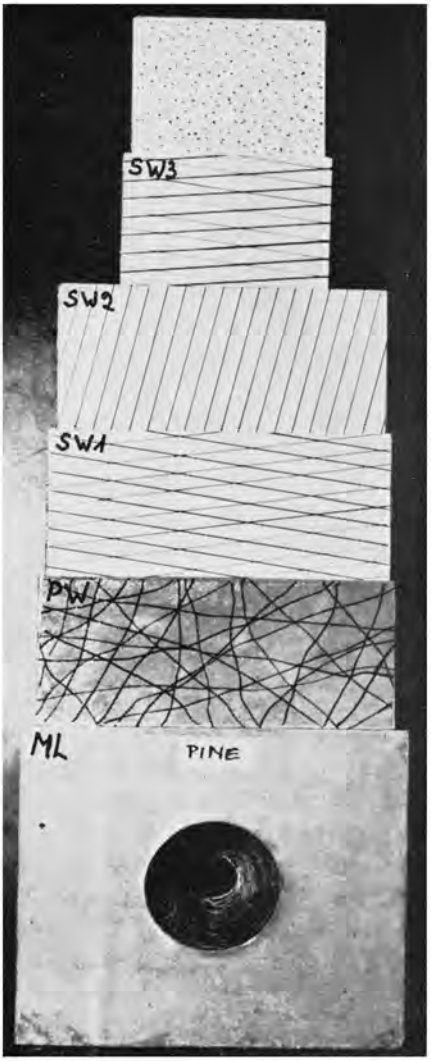

Fig. 1—Schematic model of a pine tracheid

These layers are shown in Fig. 2–5. Fig. 2 refers to the primary wall of a pine sulphate pulp with its typical loosely woven texture; the primary walls of plants were investigated by electron microscope technique, especially by Frey-Wyssling and co-workers[21–24] and Roelofsen.[25–26] Fig. 3 shows the layer S1 with the texture as described above. This outer layer of the secondary wall, of course, becomes visible only after the primary wall has been removed. In Fig. 3, remnants of the primary wall are easily recognised. This outer, densely woven layer has been described by Emerton and co-workers[27,28] in its influence upon beating resistance and sheet formation. It is the same layer that causes the well known 'ballooning' of conifer tracheids during swelling or dissolving.[26,29] Wardrop[30] considers this layer to be composed by two layers of microfibril bundles of varying thickness; Jayme and Fengel,[20] by means of electron micrographs on ultra-thin sections of spruce tracheids, found indications that this may be a general principle, but could not verify it definitely. Fig. 4 shows the typical texture of the inner secondary wall of a spruce sulphite papermaking pulp, revealed after beating the pulp to 58° S.R. In wood and in pulps that have not been beaten, the order of the microfibrils is still more strictly parallel than in the picture shown. Finally, in Fig. 5, the tertiary wall is shown through an open bordered pit. This inner layer has been very thoroughly investigated by Bucher[31–33] and, recently, with the electron microscope by Wardrop and Dadswell,[34] Nécesaný[35] and Liese.[36]

Fig. 6, taken from investigations by Jayme and Fengel,[20,37] gives an indication of the relative thickness of the four cell wall layers discussed as revealed by electron microscope investigations of ultra-thin sections of spruce early wood tracheids. On an average, the primary layer takes up about 10 per cent of the total wall, S1 about 8 per cent, S2 about 78 per cent and S3 only about 4 per cent. It will be shown later on that all the three layers P, S1 and S2 are able to take part in fibre bonding.

Effects caused by drying

THE final strength of a fibre sheet is developed by drying. During this process, a number of effects are taking place decidedly influencing the ultimate sheet strength[30] such as *shrinking* of the formerly swollen fibres, combined with internal irreversible *hornification*,[39,40] the extent of which has been quantitatively measured by Jayme and co-workers[41–44] by means of the water retention value, combined with the formation of *hydrogen bonds*. Another sum of effects is related to the surface of the cells forming the sheet, which

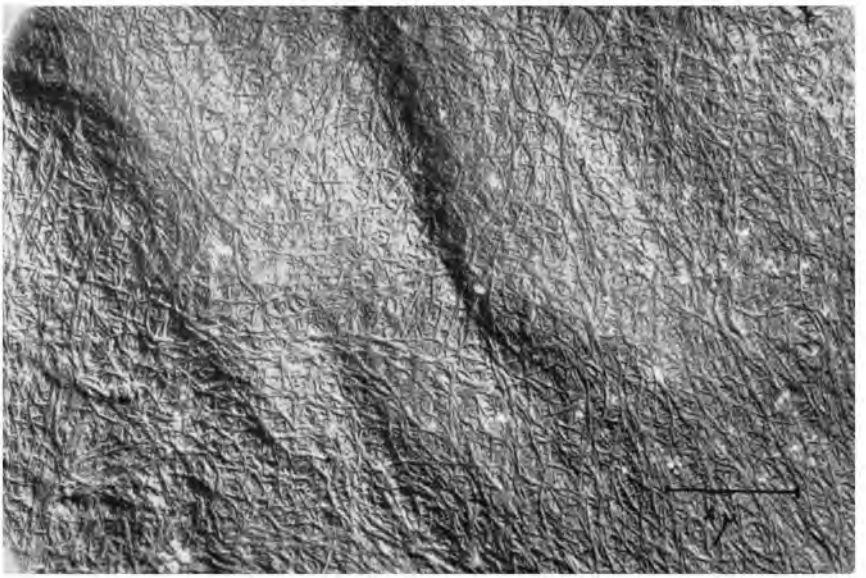

Fig. 2—Primary wall of a pine tracheid in a sulphate pulp

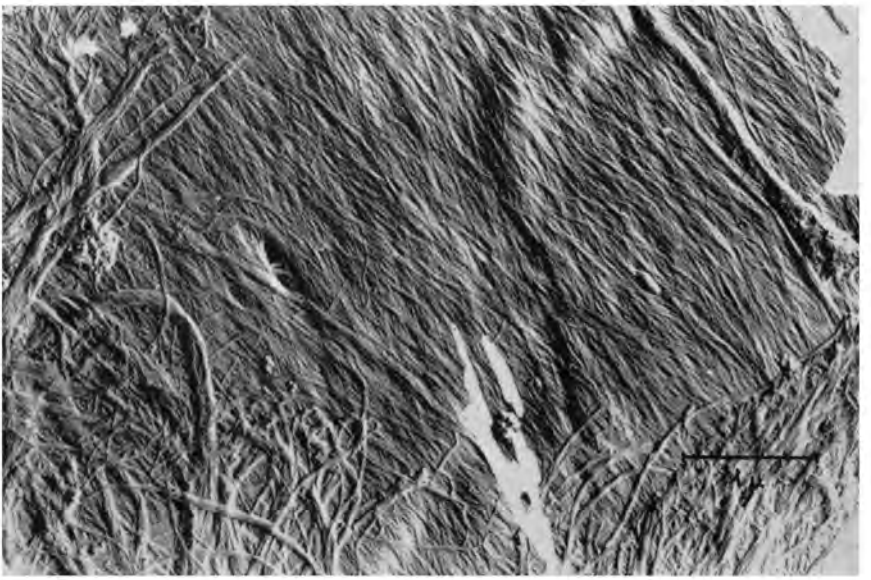

Fig. 3—Outer secondary wall in a pine sulphate pulp with superimposed remnants of the primary wall

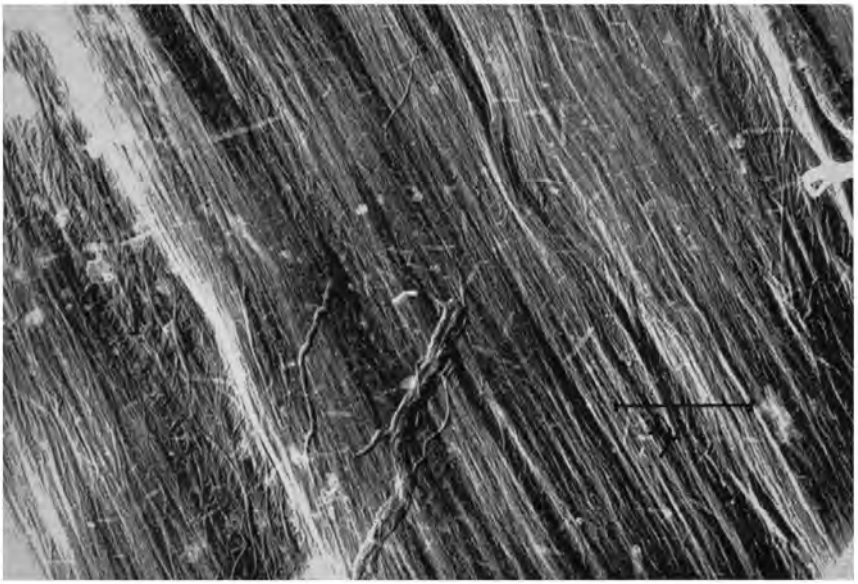

Fig. 4—Central layer of the secondary wall (S2) of a spruce pulp beaten for 30 min

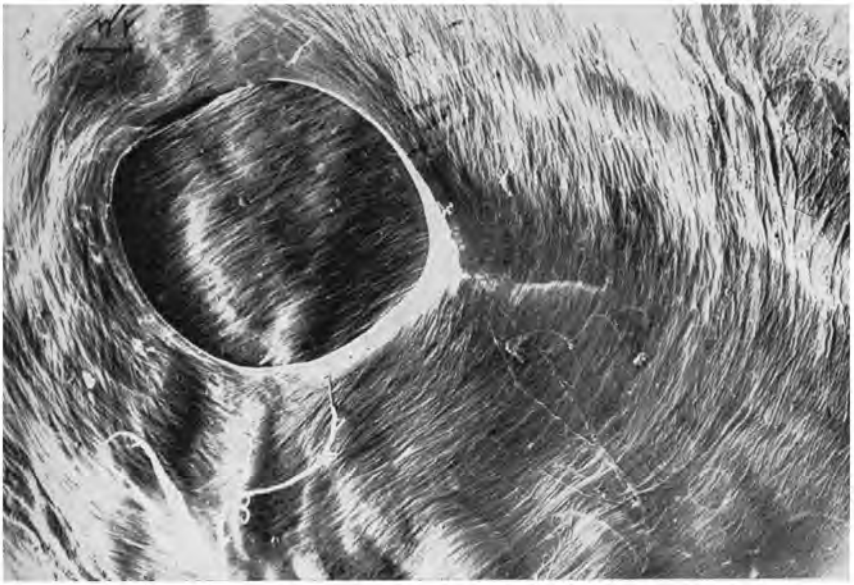

Fig. 5—Pine sulphate pulp—the tertiary wall (S3) of this collapsed tracheid can be seen through a pit aperture

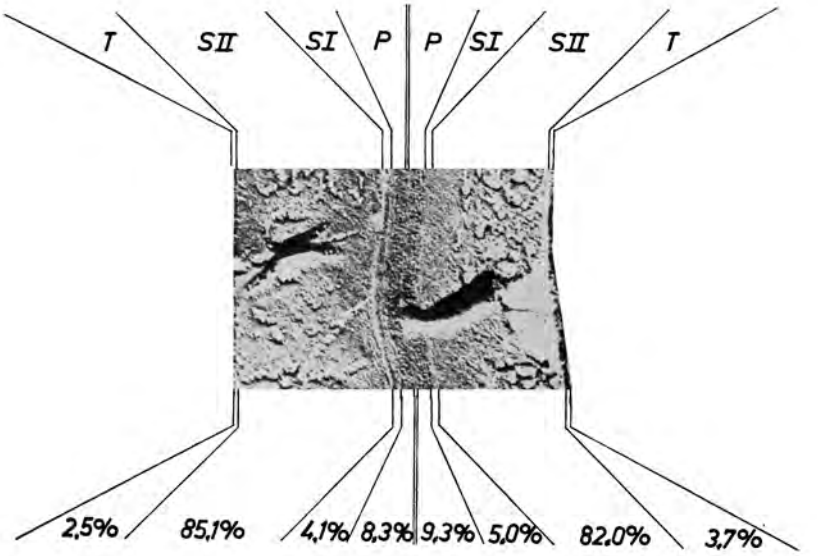

Fig. 6—Electron micrograph of an ultra-thin section through neighbouring spruce early wood tracheids showing thickness of the various cell wall layers

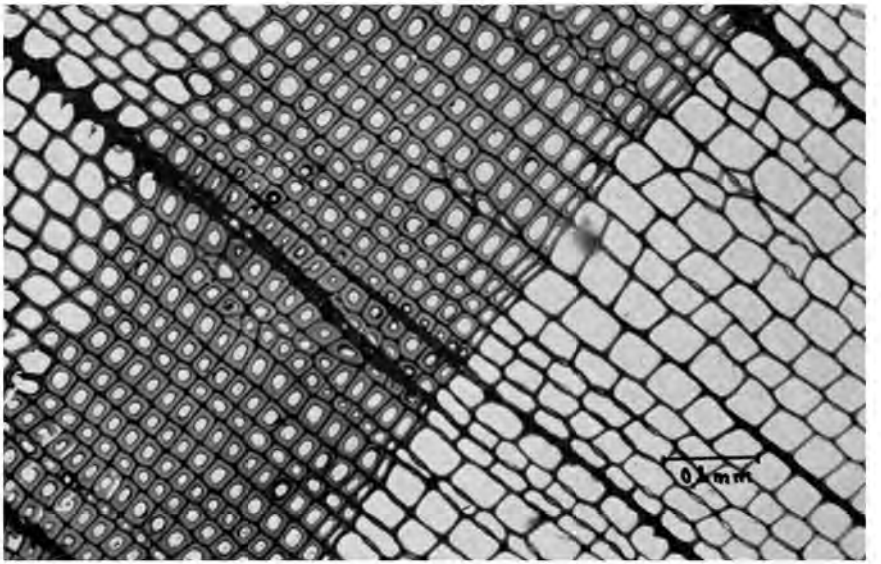

Fig. 7—Light microscope enlargement of a section through coniferous wood, showing the transition zone of early wood to late wood—most of the cells shown are rectangular in shape

again varies with the type—that is, with the texture of the cell wall layer participating in the contact and with the smoothness of the surface involved.

In coniferous wood, the tracheids originally occur as cells, the cross-section of which depicts 4–6 sharp corners (*see* Fig. 7[45]). Also to be considered is the well-known large difference between thin-walled early wood and thick-walled late wood, the latter appearing in Fig. 7 as the darker zone.

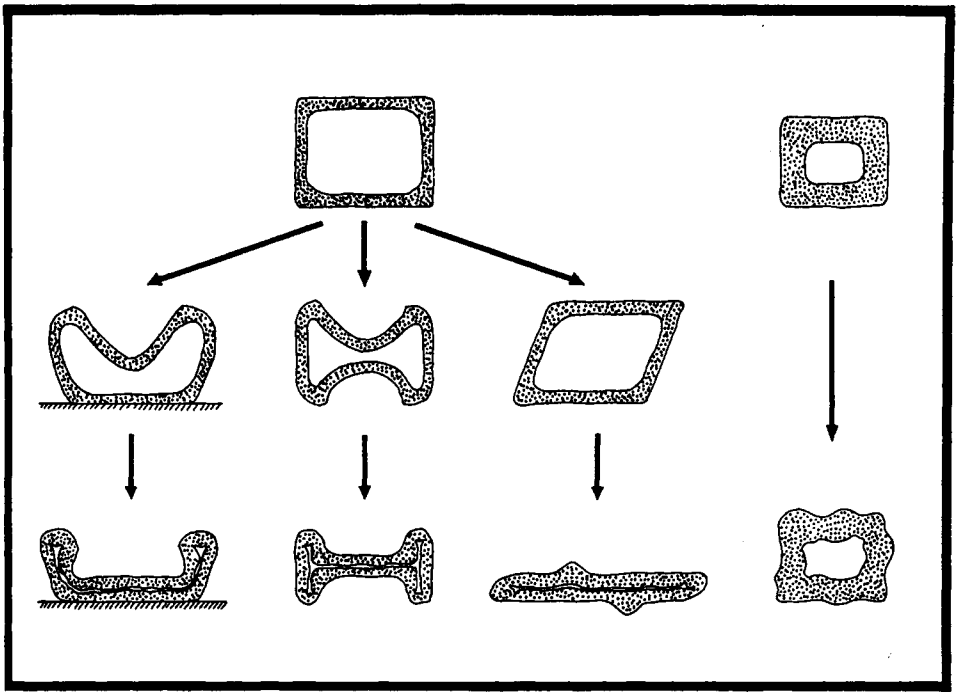

Fig. 8—Schematic drawing of the possible alterations during the drying of a rectangular early wood and of a late wood fibre

After pulping, this cell represents only about 50 per cent of its original substance and collapses to a ribbon (if originating from early wood) or largely retains its tube form (if originating from late wood). However, there the thick corners play a role, too. Emerton[4] has already shown schematically which types of the collapsed forms he considered may be shown by dried fibres. We have followed up these possibilities still more closely and drawn the result of our observations in Fig. 8 by means of cell cross-sections with

Fig. 9—Spruce sulphite pulp—example for formation of two side ridges (compare Fig. 8, lower left)

Fig. 10—Two fibres crossing each other and showing thrown-up ridges that prevent them from coming into a very close contact

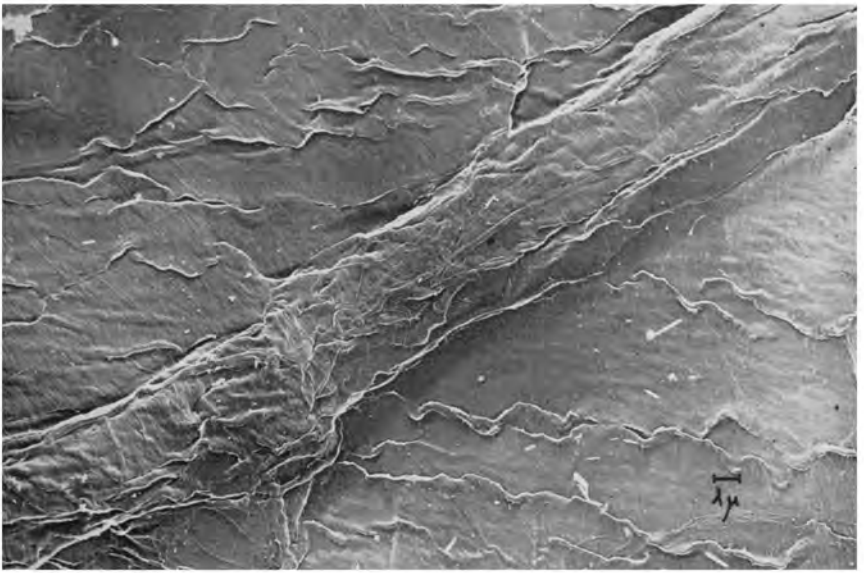

Fig. 11—Pine sulphate pulp—example of formation of ridge at a surface (compare Fig. 8)

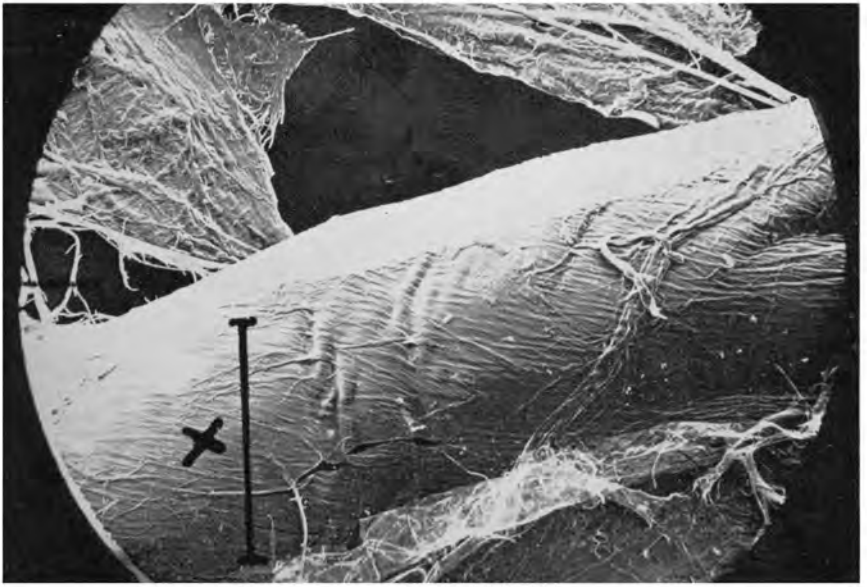

Fig. 12—Compression wood cell in a coniferous woodpulp

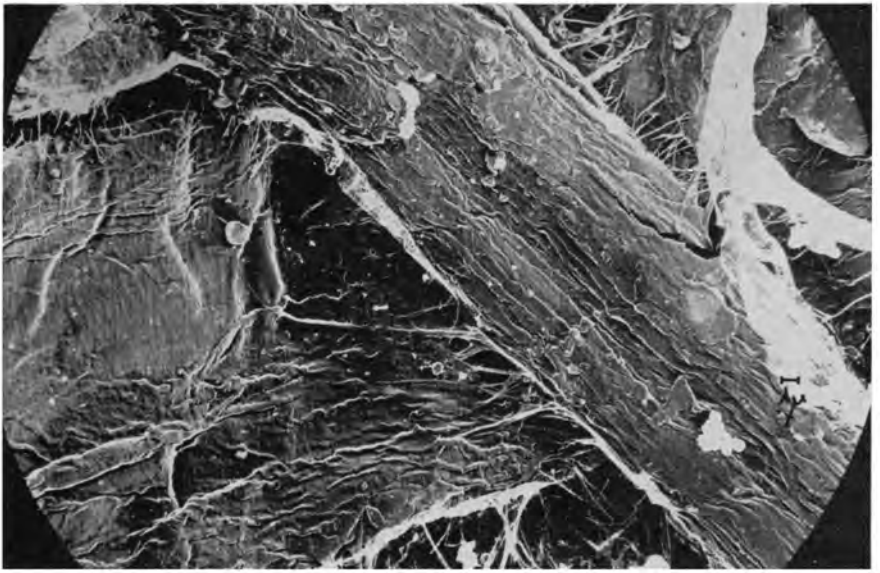

Fig. 13—Uncollapsed late wood cell crossing a collapsed early wood cell in a technical printing paper

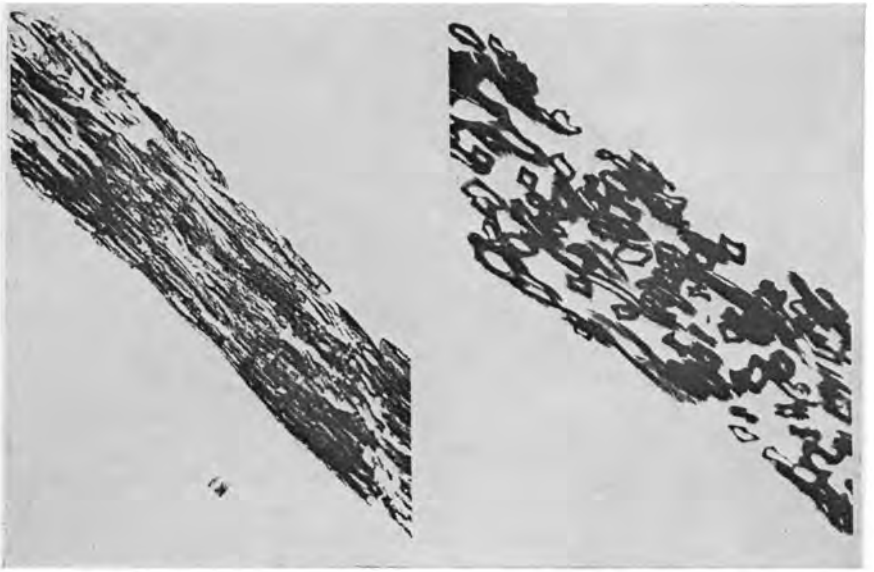

Fig. 14—Light microscope enlargement of transverse sections through pulp sheets formed of early wood and of late wood cells

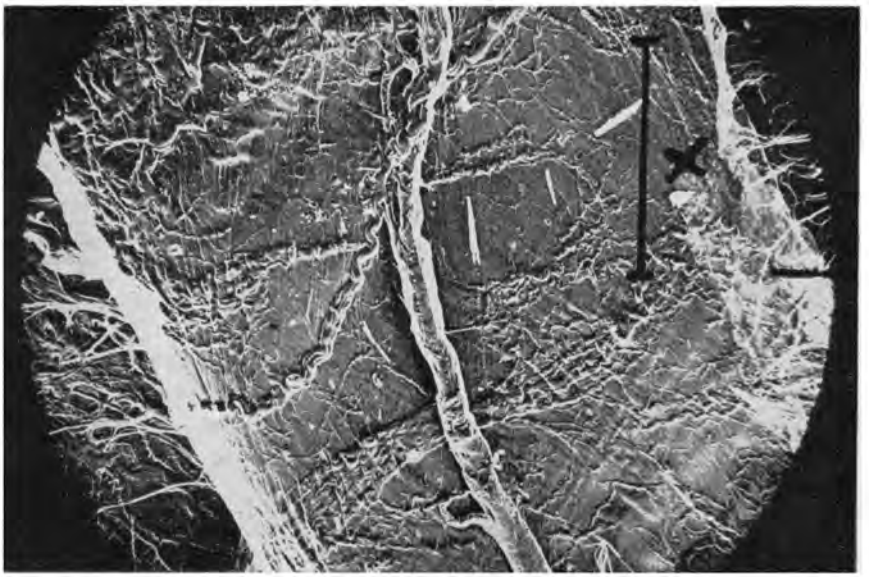

Fig. 15—Outer cell walls of a pulp fibre rolled together into a 'thick' rope and thus decreasing possibilities of contact

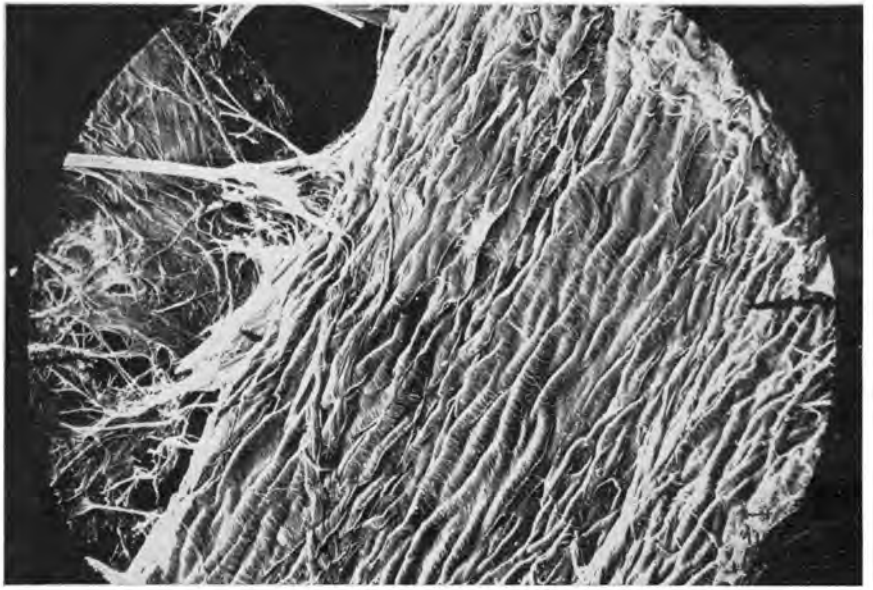

Fig. 16—Pulp fibre in a technical filter paper that has been treated with alkali—the outer secondary wall has become too large for the extracted inner layers and, after drying, shows many axially running wrinkles

four thick corners. The thin-walled early wood tracheid may on drying on to a solid substratum (such as another tracheid) throw up two walls at the sides. If the same tracheid dries without a support, its cross-section may show the shape of a double-T beam. It may also collapse similar to a parallelogram and will then exhibit a ribbon with two ridges, one at each side. The late wood tracheid with thick walls and thin lumen will hardly collapse at all and will show only a few shrinkage folds in the axial direction.

This schematic drawing is supported by the electron micrographs Fig. 9–11, part of which will be presented three-dimensionally. Fig. 9 shows an early wood tracheid with high ridges at both sides; in Fig. 10, one tracheid with a high ridge rests upon another one with a similar ridge. Fig. 11 shows such a ridge in the middle part of the surface of a collapsed tracheid.

All these structures must play a so-to-speak mechanical role during the development of fibre-to-fibre bonding. Their presence will prevent an intimate approximation of the surfaces to be bonded. A deciding role will be played also by cells that do not collapse at all such as a compression wood cell (Dadswell, Wardrop and Watson,[46] Casperson[47]), characterised by its cylindrical structure and shown in Fig. 12 or the late wood tracheids depicted in Fig. 13.

Jayme and Gessler[48] have occupied themselves recently again with the question of interrelationships between tracheid morphology and sheet strength, with particular reference to the differences between early and late wood. They prepared 'biological' pulps from pure early and late wood and tested these in several ways. Fig. 14 demonstrates on sheet cross-sections[49] the striking difference between sheets of tracheids of the ribbon (early wood) and tube (late wood) types. On close examination, all the forms shown schematically in Fig. 8 can be found. The ribbon type produces a dense sheet, whereas the tube type leads to a sheet of high bulk and high porosity. It is obvious that the latter will have the lower strength properties, at least in breaking length and burst factor.

If the primary wall is somewhat loosened up, this most probably will mean an advantage for the formation of fibre-to-fibre contacts. If, however, the microfibrils on the surface roll themselves together to a rather 'thick' bundle (as shown in Fig. 15), this will mean a new obstacle is formed, hindering close fibre-to-fibre contact.

Moreover, chemical treatment of fibres may lead to unexpected effects that will mechanically affect the approximation of the fibres. We have observed[8] that, after the alkaline treatment of cellulose fibres, owing to the loss of dissolved material, the outer cell wall layers become too wide

and, on drying on to the layers underneath, have to form very distinct and deep wrinkles in the fibre direction.

This interesting effect is shown in Fig. 16. We wanted to make certain that the explanation given is correct and therefore such alkaline-treated samples were beaten for a short time and then investigated again. Fig. 17 is typical for the result obtained. One recognises that the wrinkled surface must be part of the S1 layer, since, where it has become torn, the parallel orientation of the layer S2 is revealed.

Secondary effects caused by drying

IN the final dried sheet of paper, the secondary effects occurring during drying must have a great bearing upon sheet properties.

If isolated microfibrils in suspension are allowed to dry on a solid surface, they do not show any peculiarities (Fig. 18), although they are strongly bound to each other by secondary valency bonds, including hydrogen bonds. The same holds true for microfibrillar lamellae that are able to attach themselves to another solid surface. In Fig. 19, a bordered pit system is shown, the pit membrane of which dried on to the surface beneath it without practically any change of its primary wall type texture. If, however, such a lamella cannot affix itself to a surface but has to dry while being suspended in space severe texture alterations will occur as shown in Fig. 20. The secondary valency forces will now have to go into action laterally and, depending upon the type of the original textures, new ones will be formed such as ring-net textures out of primary walls and bundles from parallel oriented layers. We reported details about this at the Cambridge symposium 4 years ago.[50]

Primary wall bonds

UNDOUBTEDLY, the strength of bonds must be influenced by the texture of the cell wall layer taking part in forming the bond. It is well known that the presence of lignin stiffens a fibre and thus impedes sheet strength development.[41] This is one of the reasons for the poor strength properties exhibited by mechanical pulps.

Should most of the lignin present in original wood be removed by chemical pulping however, the various microfibril layers become free to divide themselves into lamellae or microfibril bundles.

Former investigations by light optics indicated that pulps showed fibrillation after a certain period of beating. This recognisable fibrillation

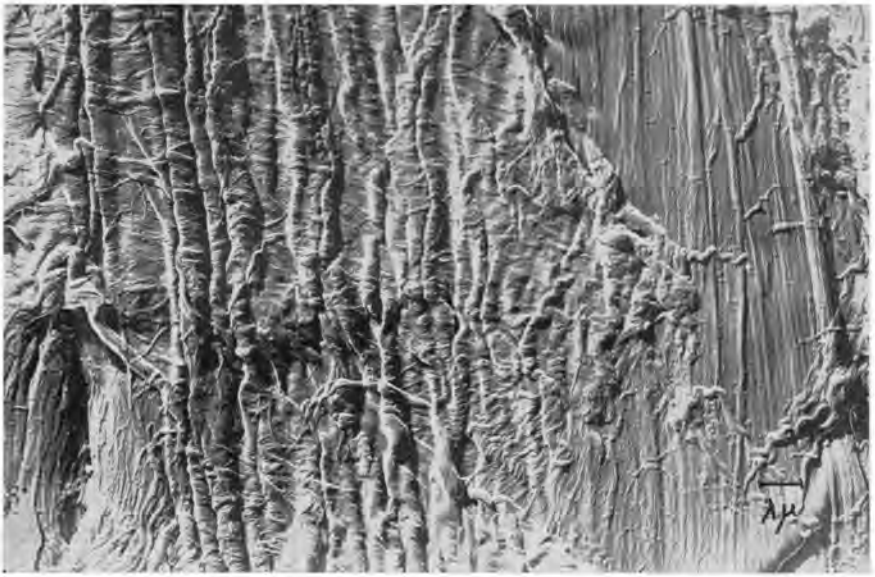

Fig. 17—Beaten pulp—the partially torn, wrinkled outer secondary wall reveals the rather flat, central layer of the secondary wall

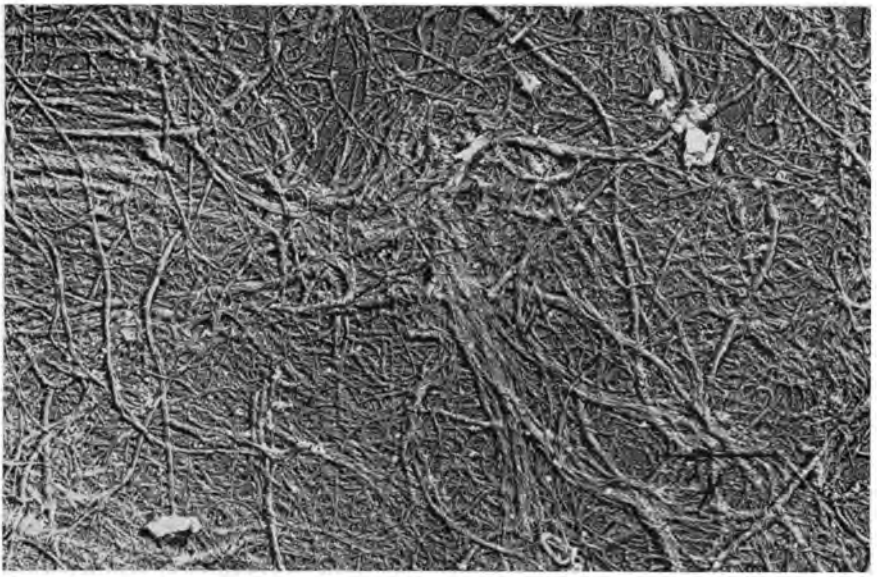

Fig. 18—Suspension of microfibrils dried on to a formvar support—besides some aggregated bundles, no drying effect is apparent

Fig. 19—Pit membrane in a sulphite pulp having dried on to the collapsed pit yard and the tertiary wall opposite—no striking drying features are visible

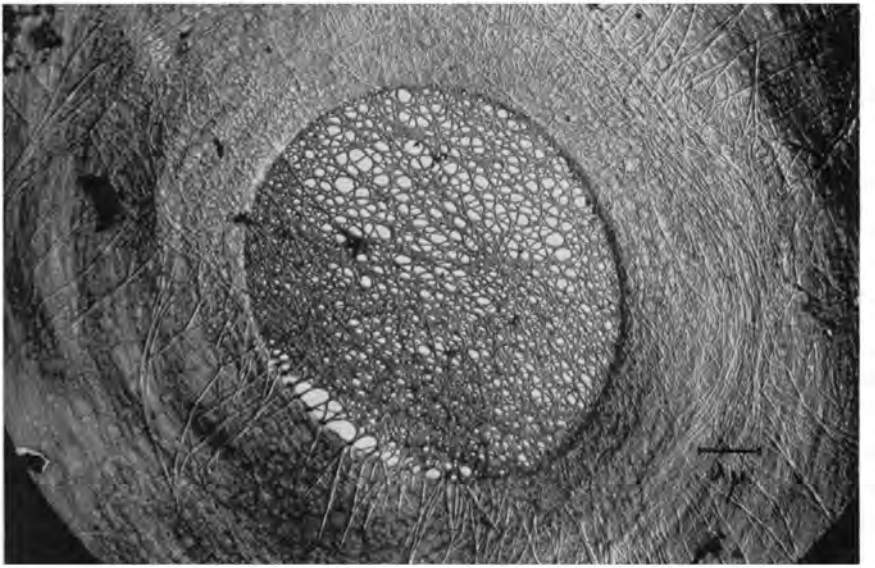

Fig. 20—Same event at a non-collapsed pit—the only two-dimensional drying forces at the free-hanging part of the membrane over the aperture have caused a side aggregation of microfibrils to form a ring-net structure

resulted from a dividing up of the inner secondary layer S2 (Asunmaa and Steenberg[9]) into microfibrils that could be detected by light microscopy. Electron microscopy was able to show in addition the existence of fibre-to-fibre bonds from the outer cell wall layers. We could show (Jayme and Hunger[51,52]) that the first layer to form bonds—as to be expected—is the primary wall. Fig. 21 depicts a lamella of the primary wall that has been torn off from the tracheid at the left lower corner, thus setting free the secondary layer S1. When the lamella is suspended in space, ring-net structures have formed during drying. Fig. 22 refers to the same type of bonding. A rather large area of primary wall has detached itself from the tracheid in the upper part of the picture and fastened itself to the tracheid below. Wherever the lamella is bound to the tracheid surface after drying, it does not show any alterations of texture; wherever it spans through space, ring-net textures are formed. This picture conveys the impression that such bonds of primary wall texture may undoubtedly be of considerable strength (*see also* below).

Secondary wall bonds

S1 bonds

AFTER the primary wall has become peeled off, the next bonds to be formed will be those by the outer secondary wall layer S1 (*see also* Cambridge symposium discussion, p. 427). In Fig. 23, the event is demonstrated that both types of bond occur side by side. At the bottom, a primary wall bond is shown characterised by its ring-net structure and, above it, a bond from the outer secondary wall characterised by the almost parallel orientation of the microfibrils. Another such bond is shown in Fig. 24. A lamella of S1 texture reaches from the tracheid at the upper left to the tracheid below and has become affixed to it by drying. An apparently rather strong bond has been formed where the lamella spans the free space.

S2 bonds

During prolonged mechanical treatment, be it during the movement of pulps through pumps or other mechanical devices or during beating, the outside layers will be torn off (forming suspensions of thin lamellae of microfibrils); then the fibrillation of the inner secondary wall layer S2 (constituting in early wood tracheids about 78 per cent of the total cell wall) will take place, which represents the one found formerly by light optics. We have established that with this a pronounced alteration of type of bonds is occurring. The bonds of primary wall and S1 type consist of thin lamellae

of fairly wide areas, whereas S2 bonds depict themselves as 'rope' or 'microfibril bundles'.

Such bonds may sometimes even form in unbeaten pulps (Fig. 25), but are most frequent in beaten pulps (Fig. 26). The very different nature of these bonds is obvious.

Relative strength of primary wall

S1 and S2 bonds

UP to now, insufficient exact data are available for distinctly classifying the various bonds by the strength they confer to the finished sheet, though there are several indications of a more qualitative nature.

Some authors[53,54] believe that the primary wall does not take part at all in strength development. However, Jayme, Kohler and Haas[55] detected pulps with extraordinary properties, the so-called 'biological' pulps, prepared by mild sulphate pulping of green wood and mild mechanical handling of the pulps produced. These showed extremely high folding properties (double folds up to 50 000!), which decreased after short beating (to 10 000, for example) and only then rose slowly again. It is evident that these very special properties must—at least in part—be attributed to bonds of the primary wall type.

Chédin[56] also points out the important role that in his view the primary wall of pulp fibres plays and mentions an experiment carried out by Renaud.[56] This author used something like hydrapulper beating, during which only the surface of the fibres is exposed to friction and in this way reached very high sheet strength. Chédin believes this to be due to a 'roughening up' of the primary walls; we would like to look upon this as partial loosening of primary wall layers, which will form finely lamellated bonds with other fibres of a rather flexible nature.

Most probably the lamellae of the S1 type also contribute to the development of sheet strength.

Kallmes[57] removed by mechanical action the primary and S1 layers of spruce sulphite tracheids; if the fraction thus separated was returned to the tracheid remnants with an S2 surface, the sheet strength increased again considerably. Besides, it may be assumed that the strange strength development trends shown by mixture of pulps of very different nature such as pulps from coniferous wood and cereal straw (Jayme and Krüger[58]) may find their explanation in this direction—by the interaction of 'surfaces' of varying type, that is, of microfibril aggregates of varying texture.

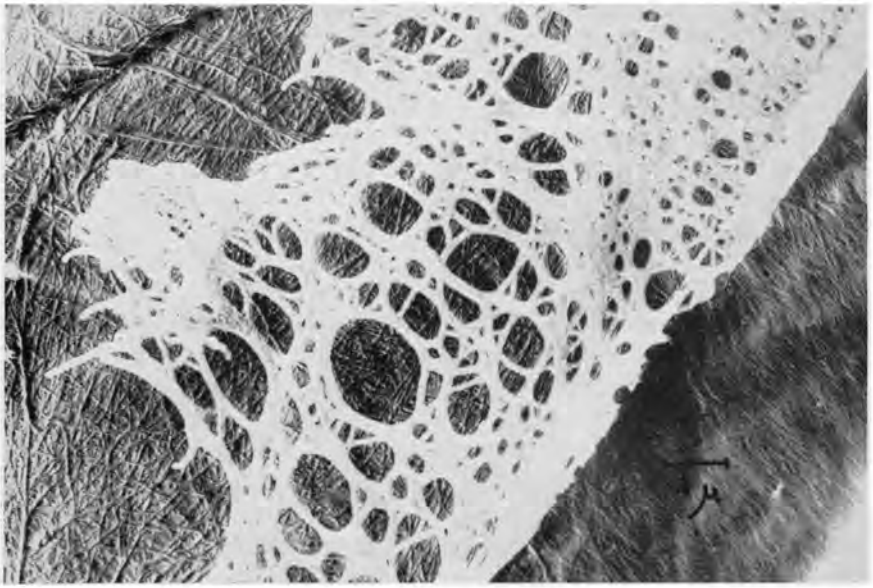

Fig. 21—A lamella of primary wall torn apart that has dried in erected position and showing hornification effects (S1 is to be seen beneath)

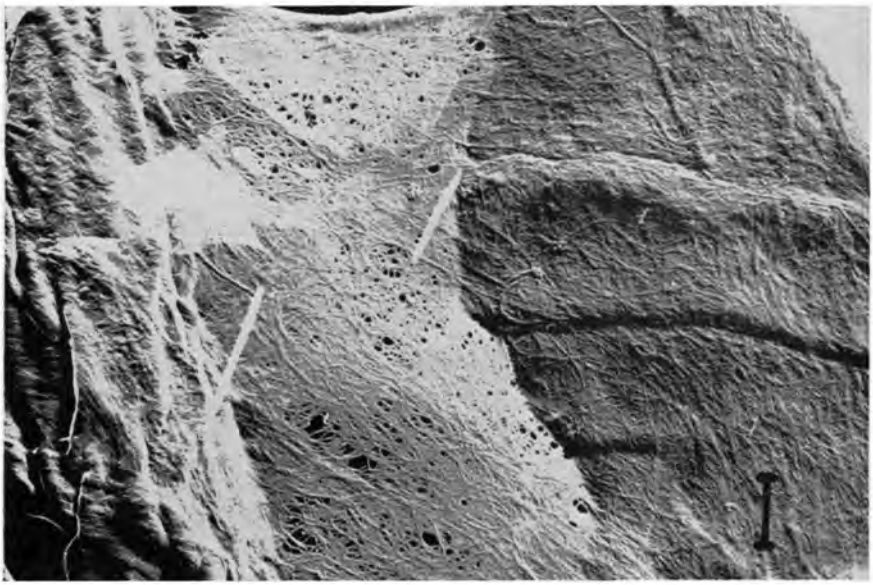

Fig. 22—Primary wall fibre bond in pine kraft pulp

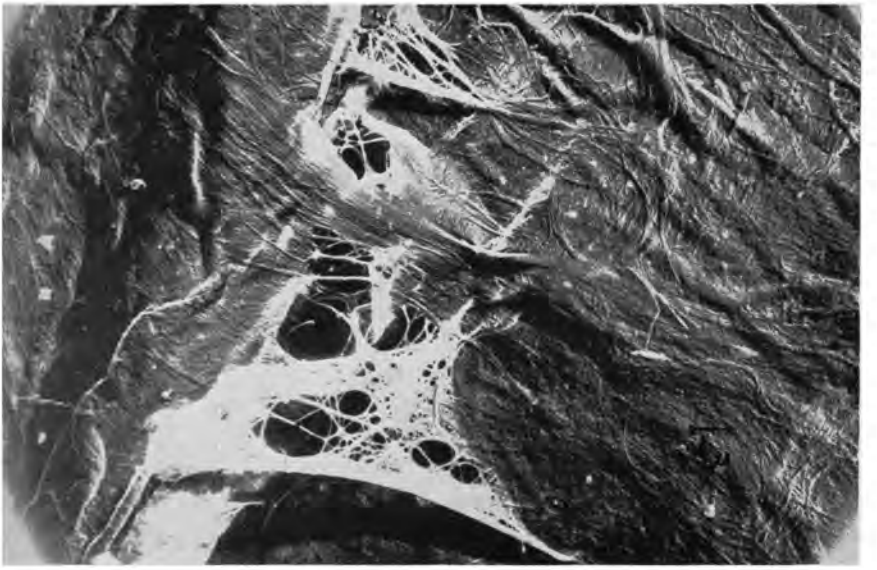

Fig. 23—Neighbouring primary and outer secondary wall fibre bonds in pine kraft pulp

Fig. 24—Lamella of the outer secondary wall of the upper fibre forms a fibre bond in a pine kraft pulp

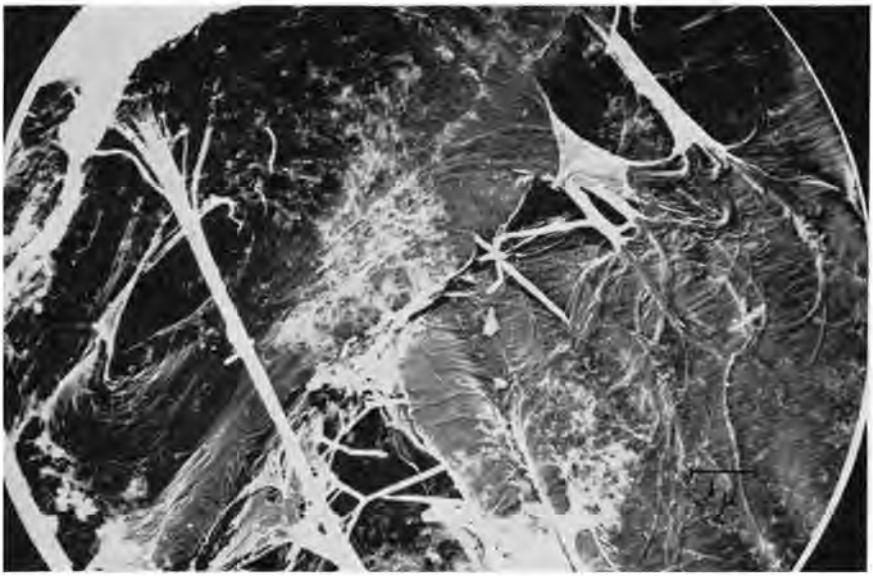

Fig. 25—Bundles of parallel-running microfibrils out of the central layer of the secondary wall forming fibre bonds in a spruce sulphate pulp (the surrounding white 'skins' result from the electron microscope preparation and have nothing to do with the pulp)

Fibre-to-fibre contact

As an important type of bonding, direct fibre-to-fibre contact has to be discussed. This type will be rather strong in the case of unbeaten or little beaten pulps. It is characterised by zones of direct contact between the fibres and, of course, subject to all the disturbances by surface roughnesses such as high ridges and wrinkles shown by us above. Fig. 27 shows such a contact zone.

These direct contact zones have been investigated by Parsons,[59] Nordman and others[60] by light optical diffraction and recently by Page;[61] the latter author uses the light microscope under conditions of polarised vertical illumination. Page and Tydeman,[62] from these observations, choose to classify the fibre-to-fibre bonds as of three types —

1. Those showing complete optical contact.
2. Contact areas limited by the intervention of a third fibre.
3. Contact areas limited by intervention other than *2*.

In view of the electron optical evidence shown by us, we believe this classification to be oversimplified, not taking into consideration the manifold other influences proved to exist. After all, it is not 'surfaces' that come into contact as shown by the light microscope, but microfibrils as proved by electron microscopy.

This was shown by us in the following way. Two undried sheets were joined to each other before drying, then dried and finally torn apart again.[63] The former contact zone was observed under the electron microscope and led to a series of micrographs, of which Fig. 28 is typical. There the *contact zones* were revealed as being formed by microfibrils single or partly in the form of thin lamellae. They had been joined by secondary valency forces and, during tearing apart, they also were torn from each other and partly torn themselves, combined with the breaking of primary valency forces. It may be judged that these fibres constitute 10–20 per cent of the total contact

Fig. 26—Bonding elements of secondary wall type in a beaten pulp

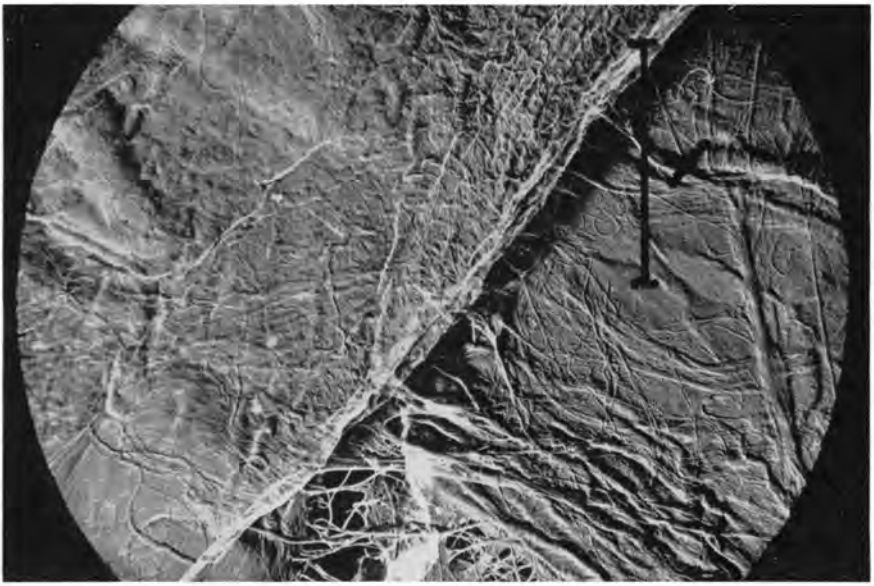

Fig. 27—Fibre flattened out and contacting the lower fibre over a wide area in a pine kraft pulp

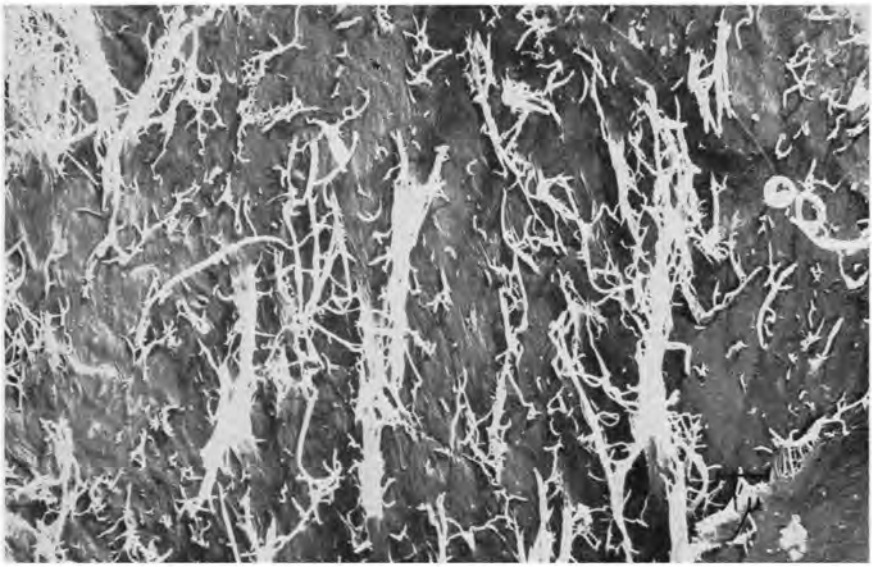

Fig. 28—Former area of contact between two fibres in a spruce sulphite pulp, made visible by tearing apart the formerly bonded fibres

area. This picture therefore refutes the conception of Page that the areas of contact represent so to speak 100 per cent surface contacts.

We believe also that the actual conditions involved in sheet formation are more complicated than is assumed by some authors: we therefore wish to show the pictures Fig. 29–32.

In Fig. 29, two fibres are seen dried upon another one and linked by microfibril bundles and lamellae. In Fig. 30, a late wood tracheid crosses an early wood tracheid; they are bonded by primary wall lamellae, as well as by direct contact zones.

Fig. 31 shows bonds in the form of strings and lamellae of primary wall and probably S1 type. Fig. 32 demonstrates the variety of bonds existing, if (besides the fibres themselves) fibre fragments are also taking part in the bonding. Moreover, some pulps may have been treated mechanically to such an extent that the texture of some of their fibres has become severely disturbed, causing the microfibrils to be in disorder and forming bonds similar to those occurring after beating (Fig. 33).

Bonding in beaten pulps

It is logical to presume that during beating the contact between the various layers within the cell wall will loosen and that with progressive beating action, therefore, first the upper, then the deeper layers of lamellae and bundles take over the bonding function. The bonding will become more frequent and in general will change from a intrafibre bond to an interfibre bond (Emerton[5]); finally, the term *fibre* looses its significance and the sheets have become practically an entanglement of microfibrils in various stages of aggregation and disaggregation.

This progress is shown by Fig. 34–39. In Fig. 34, the outside layers (primary wall and S1 wall) have been shorn off and the S2 wall becomes evident. This wall by further beating action is loosened up and the formerly strict parallel orientation of the microfibrils becomes disturbed (Fig. 35) more and more (Fig. 36 and Fig. 37). Finally, the state of disorder nears completion as shown in Fig. 38 and one may find a state towards the end as depicted in Fig. 39. In this very highly beaten pulp (strong papermaking spruce sulphite pulp, 84° S.R.), the microfibrils present themselves not only in a state of greatest disorder, but they have also become shortened. The obvious influence of the original texture must now be non-existent, since the microfibrils have become isolated and, only then, have they joined again to a new form, a *microfibril sheet.*

Fig. 29—Various fibre bonds in a pine kraft pulp

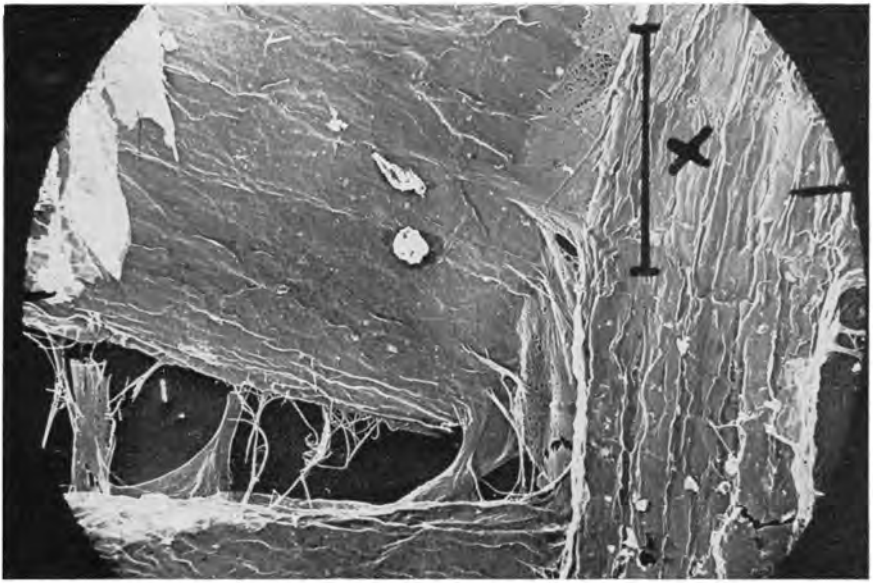

Fig. 30—Primary wall bonding lamellae between early wood and late wood fibre in a pine kraft pulp

Fig. 31—Bonding in a pine kraft pulp

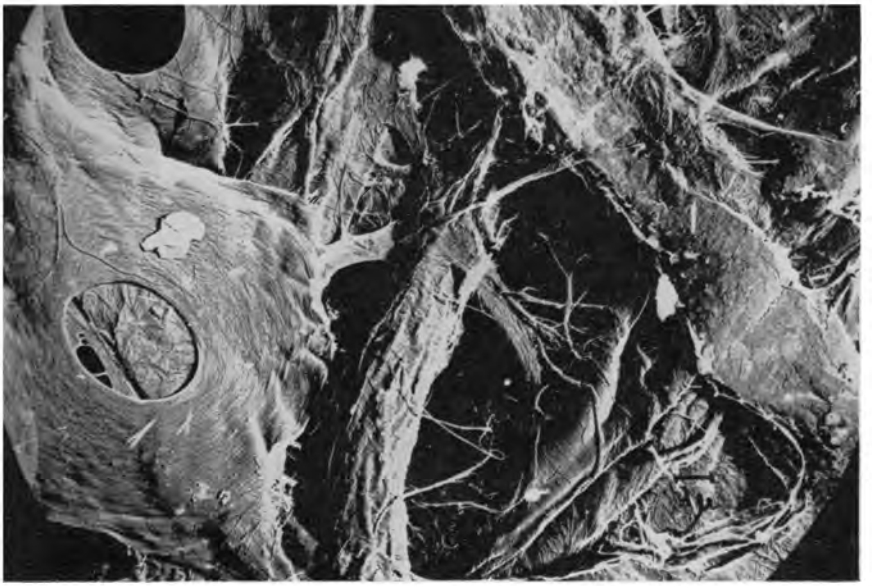

Fig. 32—Part of a pine pulp sheet showing bonded fibre fragments

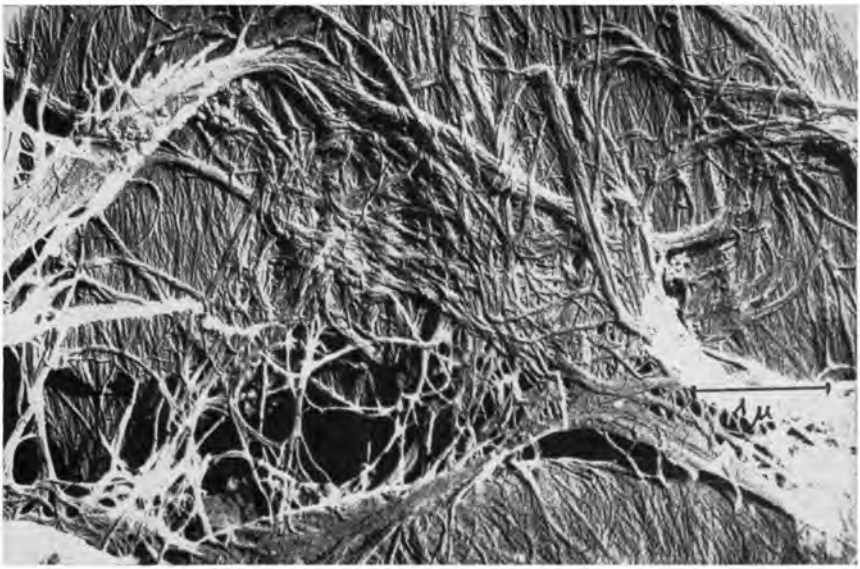

Fig. 33—Pine pulp fibres severely damaged during pulping and approximating to the interfibre bonding of a beaten pulp

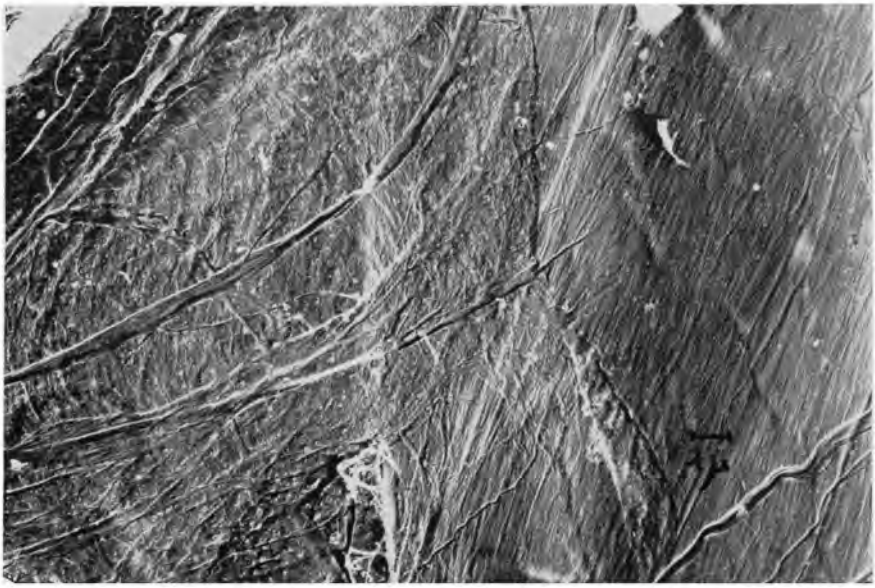

Fig. 34—Spruce sulphate pulp, beaten to 48° S.R.

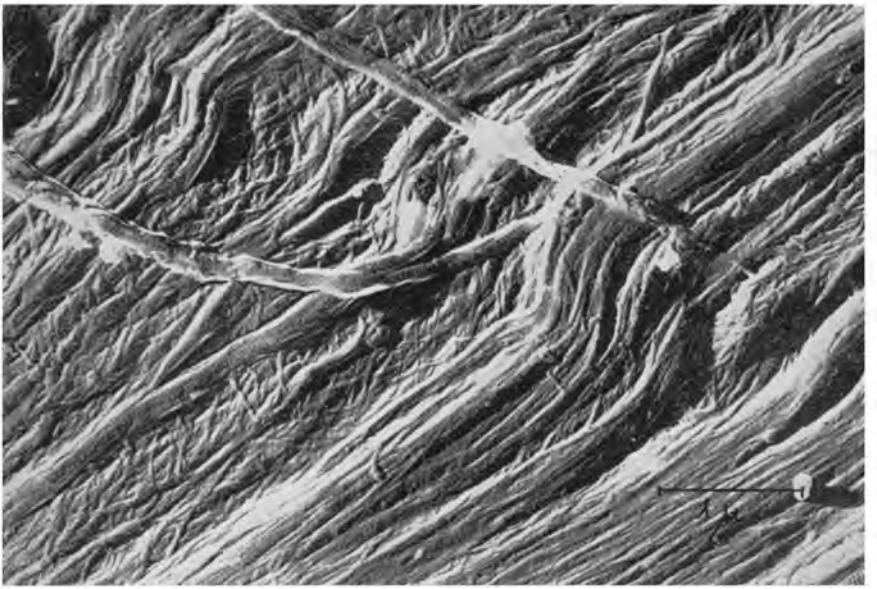

Fig. 35—Spruce sulphite pulp, beaten to 50° S.R.

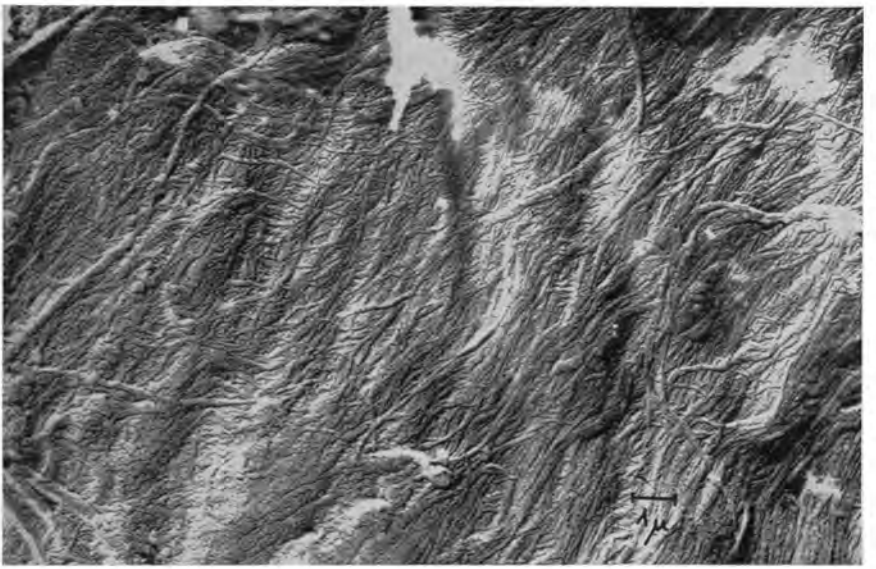

Fig. 36—Sulphate pulp beaten for 70 min and showing the state of disorder of the S2

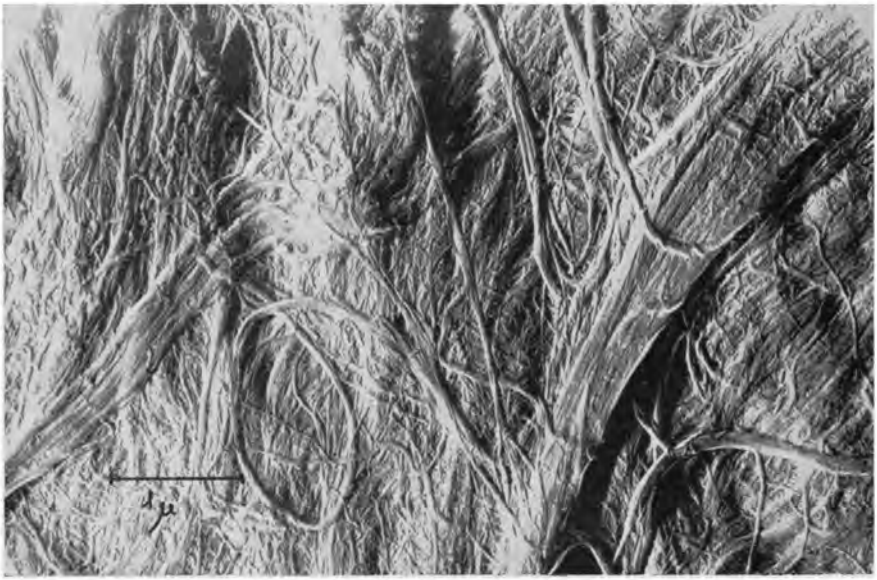

Fig. 37—A part of a 30 min beaten spruce pulp, in which the disorder of the S2 has advanced very much

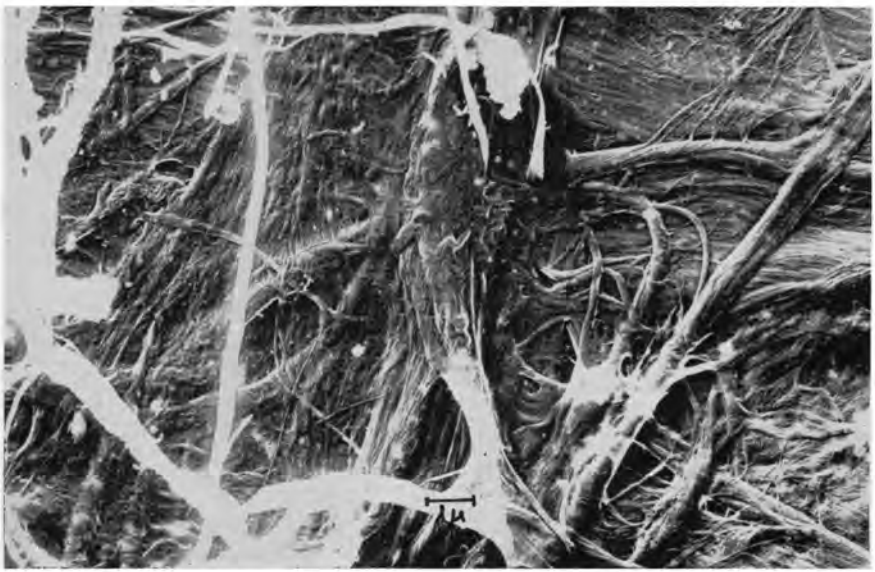

Fig. 38—High disorder of formerly textured fibre wall remnants—the pulp sheet loses the character of a fibre sheet

Fig. 39—Spruce pulp beaten to 84° S.R.—the parallel orientation of microfibrils of the S2 has mostly become lost and the presence of fragments indicates a mechanical shortening of microfibrils

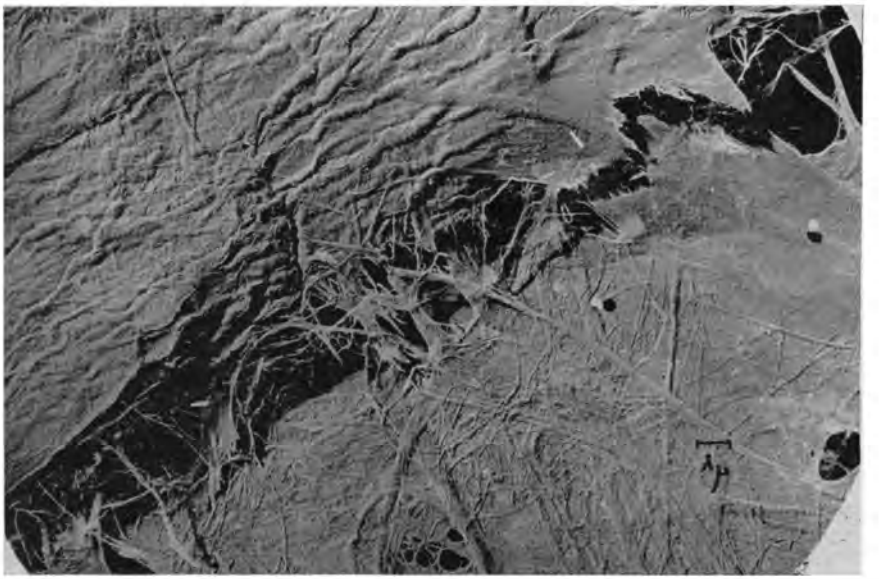

Fig. 40—Interfibre bonds in a pine kraft pulp that have been torn by shrinkage forces arising during drying

Breaking of fibre-to-fibre bonds

IT may be briefly mentioned that, during drying, it can happen that bonds formed are broken again; this will occur if shrinkage forces or other strains become stronger than the bonds existing at that time in a particular position. Fig. 40 is typical for such an occurrence: the bonds, consisting of microfibril bundles in the middle of the tear and of lamellae at the upper right, have been completely broken. These residual binding elements are rather stiff, since they have been welded together by secondary valency forces (irreversible hornification according to Jayme[39,42]); they often resemble the

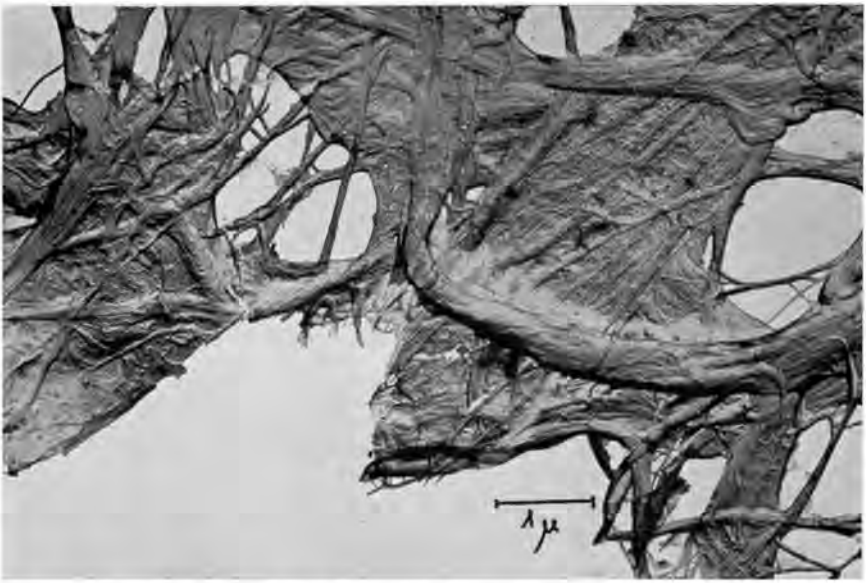

Fig. 41—Highly hornified former fibre-to-fibre bond

teeth of a saw as demonstrated in Fig. 41. This micrograph was obtained from a technical bleached spruce sulphite pulp formed into a sheet, dried, disintegrated to give a suspension and again formed into a sheet. It is obvious that such stiff microfibril aggregates lack flexibility and therefore cannot contribute to sheet strength development.

General remarks

WE have here restricted ourselves to looking at fibre-to-fibre bonds merely from a morphological point of view. We are aware of the fact that

there are many other factors influencing the ultimate strength of a paper sheet such as chemical and colloid chemical properties of the fibres and, finally, the 'own strength' of the whole fibres. Besides, during paper manufacture, a variety of further factors will play a role such as the imbedding of fillers, the pressing during water removal and general drying conditions on the papermachine.

Further research in this direction will have to change over from qualitative observations to quantitative ones—that is, studying and trying to classify the fibre-to-fibre bonds in pulps of special and determined properties—those with remarkably high or low tear factor, folding endurance and so on.

General remarks on the illustrations

ALL electron microscope specimens have been prepared by evaporating contrast metal at an angle of 25° on to the specimen, by fortifying the metal layer with evaporated carbon and by reinforcing both the metal and carbon layer under vacuum with polystyrene. Then the cellulose was destroyed in 72 per cent sulphuric acid and remnants of lignin removed in a 5 per cent solution of sodium chlorite. Finally, the polystyrene was extracted by benzene vapour and the remaining metal/carbon layer was collected on a copper bronze net with a mesh width of 50 microns, cuttings of which were observed in the electron microscope.

The line shown in the figures, mostly at the right corner, represents the length of 1 micron (1μ). If an X is added, it will mean 10 microns. The enlargement of the final printed picture corresponds then to the length of the 1 micron line measured in millimeters and multiplied by 1 000.

The term *fibre* will here be used in the sense of 'pulp fibre', instead of the botanically correct term tracheid.

All observations have been made with sulphite and sulphate coniferous woodpulps, partly of industrial origin, partly produced in this laboratory.

Summary

AN attempt has been made to classify fibre-to-fibre bonds on the basis of the texture of microfibrils involved in forming these bonds by means of 2- and 3-dimensional electron micrographs taken with our own technique.

At first, the known great differences in the original texture of the various layers of tracheids from coniferous origin are shown including the primary wall, the outer and inner secondary wall and the tertiary wall. Since the ultimate strength of a sheet is developed during drying, the secondary

alterations of the texture of parts of the cell wall layers caused by drying have been studied. Secondary valency forces can become active laterally chiefly in two ways. If such fragments find other cellulosic support, they will dry to it unchanged. If, however, they have to span free space, fragments from the primary wall will form ring-net structures, from the outer secondary wall rather parallelised microfibril lamella-like structures and from the inner secondary wall microfibril bundles.

During drying, special roughnesses are formed on the tracheid surfaces characterised by ridges already preformed in the wood and by wrinkles if chemically treated previously. These are apt to impede the fibre-to-fibre bonding process. In addition, the very great difference existing between the ribbon-like early wood and the tube-like late wood fibres is demonstrated as well as the difference between bonds formed by the lamellated primary and outer secondary wall layer and the 'bundled' inner secondary cell wall layer.

It has been proved, too, that actual microfibrils are responsible for the bonding in fibre-to-fibre contact areas. Therefore, besides the extension of the contact area, the microfibrillar texture of the surface involved will also play a role. In pulps that have been produced and slushed in mild conditions the primary wall will take part in the bonding. It could be proved that during beating at first the primary wall is torn off, exposing the outer secondary wall, which in turn takes over the bonding; after removal of this layer, the inner secondary wall separates into microfibril bundles and most of the fibre-to-fibre bonds are of this type, since this wall constitutes by far the larger part of the cell wall—say, 78 per cent of the total wall of an early wood tracheid. The isolated microfibrils, lamellae or bundles will appear as fines and, as such, will again take part in fibre-to-fibre bonding. After very extensive beating, the microfibrils of the inner secondary layer lose their original texture more or less completely and then form on drying a completely new product, a 'microfibril sheet'. It is shown that fibre-to-fibre bonds formed may be torn again during drying if they are exposed to forces stronger than themselves. It is also demonstrated that, owing to the action of secondary valency forces, the microfibrils are bonded to each other and after drying form stiff elements of little bonding action if broken apart again by disintegration of the sheet. This 'irreversible hornification' constitutes the reason for the fact that a sheet made anew from a previously dried sheet always exhibits very much lower strength properties.

The authors are aware of the fact that there are many other factors determining the final strength of a paper sheet such as chemical, colloid chemical and physical ones.

On the other hand, fibre-to-fibre bonds as the weak link of a chain will always demand attention when sheet strength is concerned. It appears necessary to elucidate the many still open questions by carrying out research work in a quantitative manner—by studying the fibre-to-fibre bonds in sheets with well-known strength data and in pulps with definite chemical and colloid chemical characteristics.

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DISCUSSION

PROF. G. JAYME: Hunger and myself wish to congratulate Page and his co-workers on the very interesting results they have obtained. However, on account of the evidence obtained by us, it would appear that the 'optical contact areas' shown by Page contain numerous parts where the contact is not 'optical'. The areas are not black throughout, but show grey and even white spots. We are inclined to believe therefore that all types of bond including bonds by microfibril lamellae and 'strings' are present in these areas.

MR. D. H. PAGE: The light microscope technique itself is not easy. There are many reasons that these areas should not appear black, simply because of the local optical conditions. Light is scattered and reflected within the fibre throughout which the observation is made and from fibres below and around it. I have dealt with all these contrast effects in my first publication on this subject.

When we have a springwood fibre collapsed, however, we have the ideal optical condition for looking at bonded areas; then we find that the areas are uniformly black in spite of the surface roughness of the fibres. I agree there is room for disagreement to some extent here; but, because there is light and shading, it does not disprove our contention. I agree the onus is on us to prove that it is good contact and our electron microscope work has done that.

MR. H. W. EMERTON: I would add to this remark that at every interface there will be a measure of depolarisation. Some of the incident plane polarised light will become elliptically polarised and this will not be extinguished by the analysers.

PROF. H. W. GIERTZ: When we speak about the adhesion between fibres in the contact area, we should also pay attention to the quality of the surface material. We have spoken mainly about microfibrils on the surface, but there may also be some hemicellulosic material there that could drastically change the behaviour at the contact surface. If these hemicelluloses are swollen and partly dissolved, they will give rise to very strong adhesion forces when the water is removed by drying and they will act as an adhesive. The amount of such surface hemicellulose will depend on the way of preparing the fibres (*see* p. 605).

MR. P. H. J. ABBOTT: What is the effect of moisture content on optical contact? One would imagine that, as the moisture content went up, the area in optical contact would increase and that this would be associated with a loss of mechanical strength. On this basis, the use of area of optical contact as a measure of bonded area would appear doubtful.

MR. PAGE: It depends on what you mean by moisture content; but, considering normal ranges of moisture content due to relative humidity changes, no effect has been observed. There is no basis therefore for any doubt.

PROF. J. D'A. CLARK: Because of surface tension forces, surfaces fibrillated when wet will appear smooth after drying. There is thus danger in observing photomicrographs of dried fibre surfaces as smooth when in reality, before drying, they were covered with fuzz and fibrillae that contributed to the bonding. There appears no evidence of fibrillae on the outer surface of a primary wall in water with a silvering technique, but this becomes apparent on the secondary wall immediately the primary wall is removed. This explains the rapid increase in strength of unbeaten fibres with beating.

A DELEGATE: Surprisingly, the same weight of a high yield pulp (about 70 per cent yield) has the same wet web strength as has a normal (perhaps 50 per cent) yield pulp on a papermachine in the same admixture with other pulps. Since there are far fewer fibres in the 70 per cent yield pulps for the same percentage weight in a mixture, some reason must be found that these fibres, present in far fewer numbers for the same percentage weight, should give such a very high proportion of wet strength. The only way to explain it is by some such supposition as Giertz has advanced that these pulps are commonly used unbeaten.

PROF. A. H. NISSAN: I wonder whether we do not sometimes create problems for ourselves by insisting on one mechanism to the exclusion of all others. Do we not really get all the different types of bond discussed today contributing to papermaking? Molecules are on all surfaces and when, through any agency, they come within certain distances from other surfaces, there will be a number of energies of interactions—electrostatic, hydrogen bonds, van der Waals' bonds, even some covalent bonds. In other words, there may be a large number of mechanisms. Sometimes, when arguing this among ourselves and each bringing evidence in support of his point of view, are we not simply unconsciously choosing evidence that illustrates the mechanism we favour?

There was a note about hemicelluloses in *Nature* this last August by Prof. Preston of Leeds University: he analyses the microfibrils and finds some differences in chemical composition between what one might call the amorphous portion and the crystallite. It is worth studying in connection with this discussion, because once again there is the possibility of different 'bonds', even between 'pure' cellulose.

PROF. B. G. RÅNBY: There is no justification for calling a hydrogen bond of the type now under discussion an ionic bond: it is not. It is actually a dipole bond. It can be argued in the case of carboxylic acids, which form two very strong hydrogen bonds. The strongest hydrogen bond we know of—for example, in hydrogen fluoride—can be ionic in nature, but this is another matter. We should call the hydrogen bonds in cellulose dipole bonds.