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PHYSICAL PROCESSES OCCURRING DURING THE DRYING PHASE

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Synopsis—A description is given of experiments designed to substantiate some facets of the authors' comprehensive theory of paper shrinkage and structure that was presented at the Oxford symposium. In particular, considerable evidence is presented in support of the basic concept in the theory—that is, the hypothesis of 'adhesion before shrinkage' of the constituent fibres. Examples are shown of a phenomenon that is the direct result of the latter process, termed *necking* of the fibres. Other factors important in the drying and shrinkage process are discussed.

Introduction

IN the theory that the authors presented at the last symposium,[1] certain observations were put forward concerning the phenomena occurring during the drying phase that were contributory to the shrinkage of the web. In addition to the behaviour of the individual fibres, something of which has already been said in this symposium,[2] the interactions *between* fibres were shown to be extremely significant in controlling the shrinkage of the sheet and in deciding its ultimate structure, hence its properties. The theory was advanced that the greatest part of sheet shrinkage has its origins in the transverse shrinkage of the fibres; but the crux of the theory was that the transverse shrinkage is communicated from one fibre to another via areas of adhesion that *develop before the final drying and transverse shrinkage of the fibres.* At a bonded crossing, the forces of transverse shrinkage of one fibre give rise to a micro-compression of the other in its longitudinal direction. Sheet shrinkage is thus associated with an actual, but *enforced* shortening of the fibres. This has been proved by measurements made on single fibres in drying sheets, which showed within experimental error that the fibres shortened in the same proportion as the shrinkage of the sheet as a whole. On the other

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hand, attempts were made to detect, by direct microscopic observation, relative fibre movement in a drying sheet, but no such phenomenon could be resolved. It is thus believed that interfibre shrinkage (compaction of the sheet or relative fibre movement), if it does exist at all, contributes only by a negligible amount to the sheet shrinkage and plays a very small part in the determination of the ultimate sheet structure. It is very likely that the interfibre forces arising from surface tension within the porous structure of the fibrillated material of a beaten sheet can contribute appreciably to the shrinkage of a sheet, but they must do so by longitudinal compression of fibres, not by inducing relative movement.

From a consideration of the drying process in terms of the new theory, one can deduce certain factors that control—or rather decide—the shrinkage behaviour of the sheet and its ultimate structure. These factors are—

1. The intrinsic transverse shrinkage of the fibres in terms of the amount of shrinkage and the force required to inhibit it.
2. The longitudinal compressional resistance of the fibres.
3. The strength and extent of the fibre-to-fibre bonding during the drying phase.
4. The amount of fibrillation that, when present, has shrinkage forces associated with it.

Since the publication of the theory, a more detailed study of these factors has been undertaken and studies of the shrinkage of fibres have been reported elsewhere.[2,3] The results showed that the potential shrinkage of fibres is, without doubt, large enough to produce the sheet shrinkage and that it increases with beating.

Results are now presented of the examination of the validity of the 'adhesion before shrinkage' hypothesis and an experiment reported that was designed to measure the variation with beating of the compressional resistance of fibres.

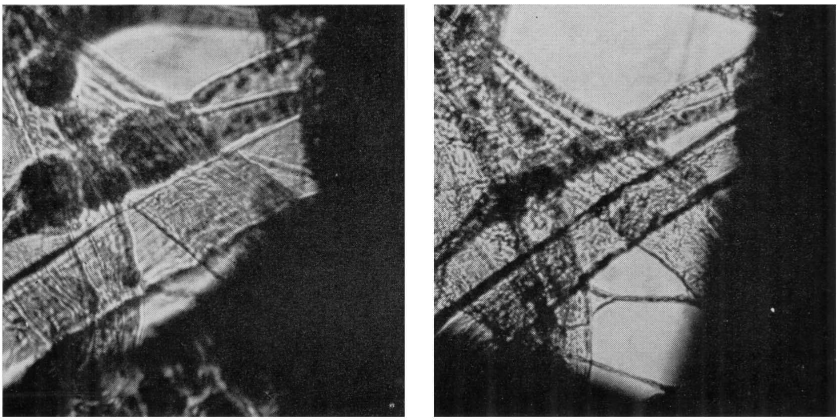
Formation of bonding during the drying phase

THIS has been studied from the aspect of the observation of phenomena associated with the contacting of two wet, swollen fibres; their subsequent drying, shrinkage, adhesion and the formation of their area of contact. It has been studied in the case of two virtually individual fibres approaching each other and in the case of fibres contacting in webs of usual substance.

Direct observation of bond formation

Using the method of polarised vertical illumination[4] for revealing contact areas (which it is assumed are the regions of bonding), the development of bonding, as well as fibre dimension changes, has been recorded by microphotography, both still and ciné.

The method for observing bond formation between individual fibres, was as follows. A wire gauze (100 wires per inch) was placed on a suitable holder consisting of a block of brass, with a hole of about ½ in diameter, which was placed on the microscope stage. A drop of dilute fibre suspension was put on to the gauze. Superfluous water was removed by soaking it away with a piece of blotting paper from underneath, leaving behind a large water meniscus containing fibres. The retention of the fibre suspension by the wire gauze is illustrated in Fig. 1, which shows fibre crossings photographed in the



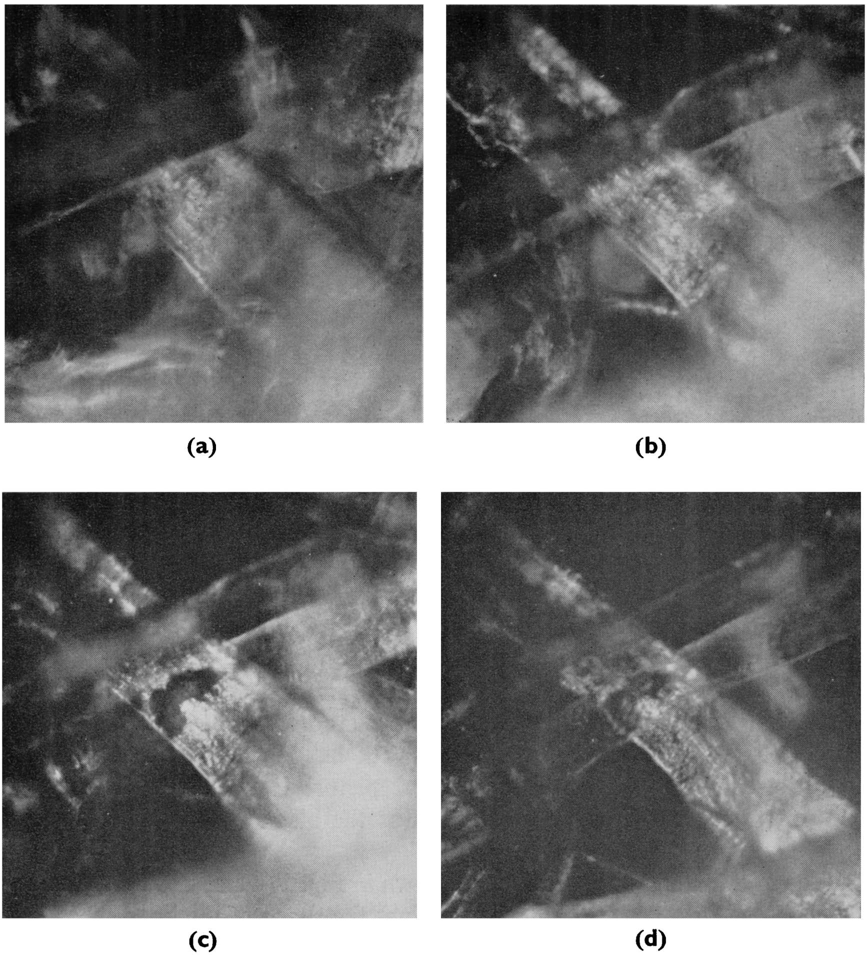
(a) (b)

Fig. 1—Fibres that have been deposited on a wire gauze for the purpose of studying the formation of their bonding while they dry (the black areas being the grid wires)—(*a*) wet, (*b*) the same fibres dry [× 300]

microscope under normal conditions of transmitted illumination. The fibres were then allowed to dry while being photographed under conditions of polarised vertical illumination.

In Fig. 2 and 3 are shown some of the micrographs taken during the drying sequence of two fibre crossings. The first picture of each series shows the fibres still immersed in a water meniscus. The last picture shows them in the condition of being air-dried; in this last picture can be seen the area of contact (or region of bonding) revealed as the black area in the otherwise relatively bright fibre.

The development of the bond area shown in Fig. 2 (which shows one of the crossings of Fig. 1) is extremely interesting; the shape of the bond when dry can be seen in the last picture (Fig. 2*d*), but very nearly the same shape is to be observed in Fig. 2*c*, when the fibres are still apparently in the condition of being swollen and presumably contain considerable moisture. In going from the state shown in *c* to *d*, the uppermost fibre has shrunk transversely by approximately 15 per cent and, in so doing, the *geometrical shape* of the black area (where contact occurs) does not undergo any significant change, but it diminishes in size in approximately the same proportion as the fibres. The change in the geometry of this crossing is represented in Fig. 4. Conceivably, this effect of the 'bond' retaining its shape, but diminishing in size, could be explained either by the loss of a water meniscus that existed between



(a) (b) (c) (d)

Fig. 2—Successive stages in the drying of the fibres of Fig. 1 photographed under conditions that reveal the bonding [× 300]

the two fibres or by the loss of bonded area. If one or other of these mechanisms were taking place, it would have to occur in the precisely required geometrical fashion that is observed.

This seems too coincidental and a more likely explanation is to be found in the theory of 'fibre adhesion before shrinkage' that was referred to in the introduction. The contact area to be observed in Fig. 2*c* was indeed the region of bonding between the two fibres, which were still in the swollen

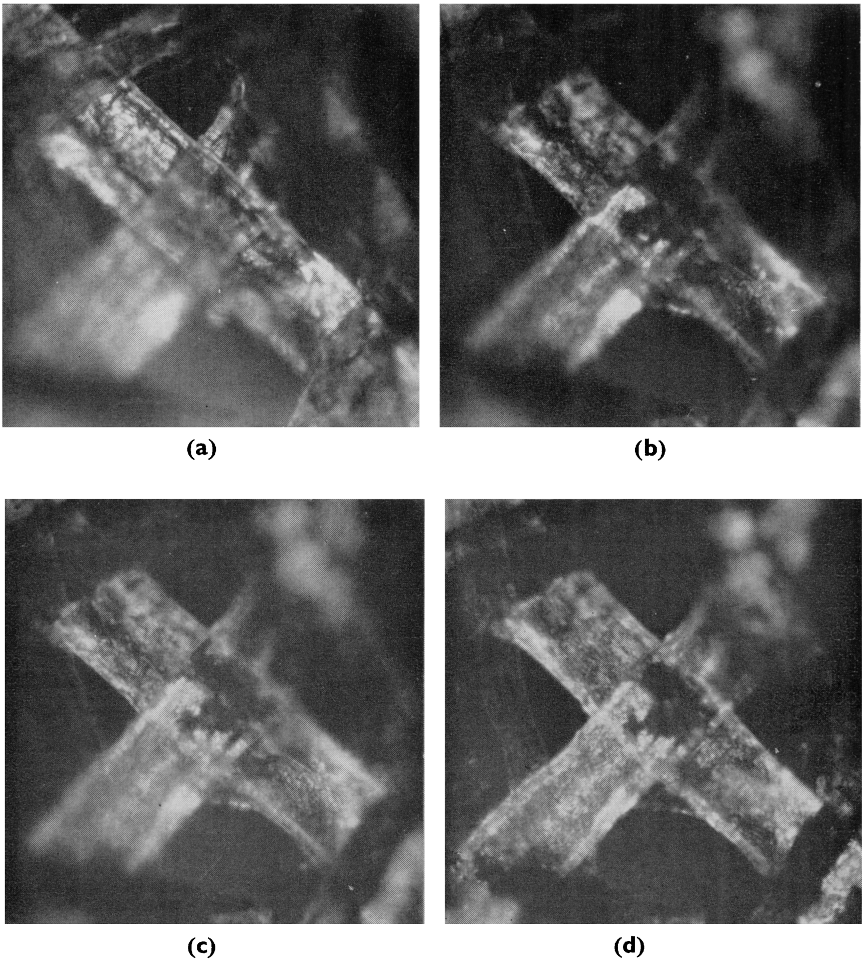


Fig. 3—A second example of the formation of the bonding between two fibres [× 300]

state. When the fibres dried and the upper fibre shrank transversely, the bonded area remained, but accordingly had to shrink with the upper fibre; this automatically implies that, as a result of the shrinkage forces of the upper fibre, the lower fibre was under compression via the bond. Furthermore, as the bond area diminished in the direction parallel to the transverse dimension of the upper fibre, it is deduced that in this example the lower fibre provided very little resistance to being compressed.

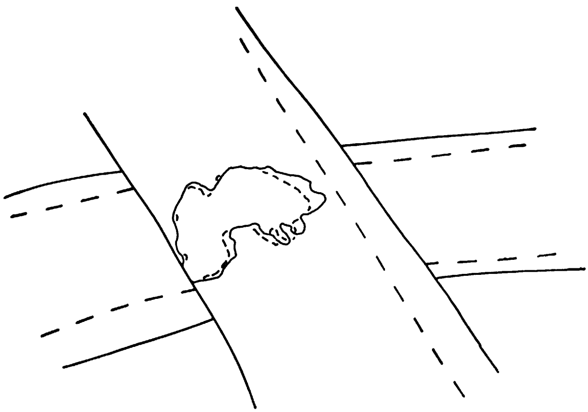


Fig. 4—Representation of the field of Fig. 2*c* and *d*, depicting the bonded area and the fibres when swollen (full lines) and when dry (broken lines)

In the second sequence (Fig. 3), the development of the final bond shape can again be seen, but the behaviour is somewhat different from that illustrated in Fig. 2. In this second case, when going from stage *c* (where the bonding has already taken on its final form) to stage *d*, during which time the fibres apparently dried and showed slight transverse shrinkage, the area of contact itself did not display any large change in size. The changes that resulted during the shrinkage stage gave rise, in this example (Fig. 5), however, to a phenomenon that has been termed *necking*. The reason for its occurrence is that, whereas outside the region of the bond site the fibres were free to shrink transversely, within the bond site, where adhesion commences *before* the shrinkage, the fibres met a significant resistance, acting against their shrinkage and arising from the compressional stiffness in the longitudinal direction of the other adhering fibre. The existence of the phenomenon of necking confirms the theory of fibre adhesion before shrinkage and the importance in the shrinkage process of the concept of the longitudinal compressional resistance of fibres.

Additional evidence for the existence of these phenomena has been obtained by ciné micrography of the formation of bonding; unfortunately, it is possible to show in print only a very small selection of stills from the ciné films to be shown at the symposium. A sequence is illustrated in Fig. 6 that again shows four stages in the drying of two fibre crossings, the formation of

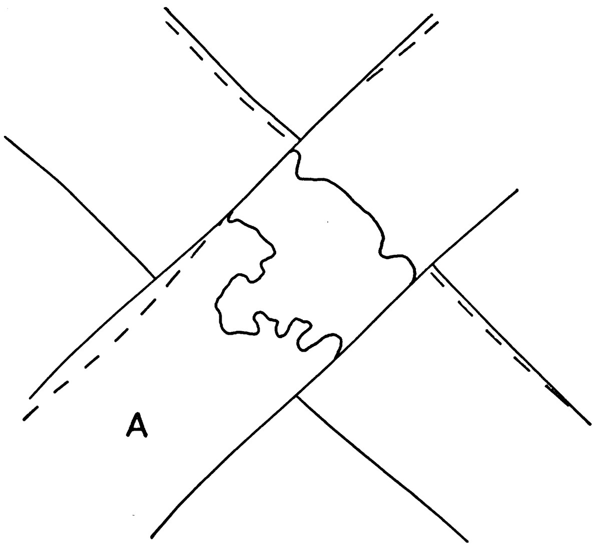


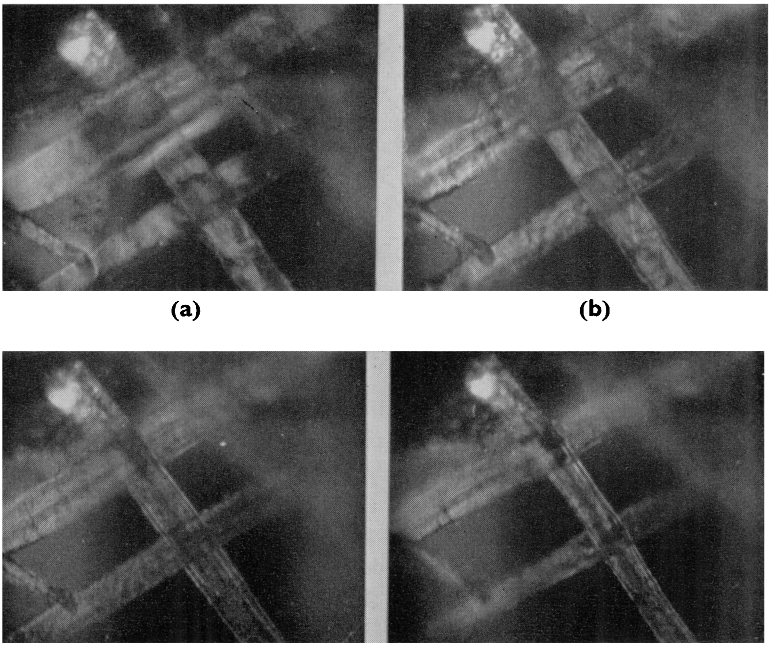
Fig. 5—Representation of the field of Fig. 3*c* and *d*, depicting the bonded area and the fibres when swollen (full lines) and when dry (broken lines): fibre *A* shrank transversely to a greater extent outside the bond site giving rise to a necking effect

the bonds between them and the final transverse shrinkage of the fibres. The tendency for the fibres to neck can again be detected. The transverse shrinkage of the fibres outside the region of the bonds is estimated to be 20 per cent. This ciné sequence—and others besides—clearly demonstrate by virtue of the movements occurring that the fibres do bond together before undergoing the largest and final part of their shrinkage.

Bond formation between model fibres

Further studies of bond formation have been made by means of model fibres that were designed not only to simulate as closely as possible the properties and behaviour of natural fibres, but also to have the advantage of being larger and more uniform. This was achieved by using regenerated cellulose film as the material from which the models were made.

Thin cellulose film (25 μ thick) was cut into pieces 1 cm long and 200 μ wide. This, on the basis of a linear magnification of five times, was an idealised representation of a collapsed fibre 2 mm long and 40 × 5 μ in cross-section. Machine-made cellulose film normally possesses a high degree of anisotropy, similar to machine-made paper. In particular, the swelling and shrinkage in the plane of the sheet varies with direction. When the material



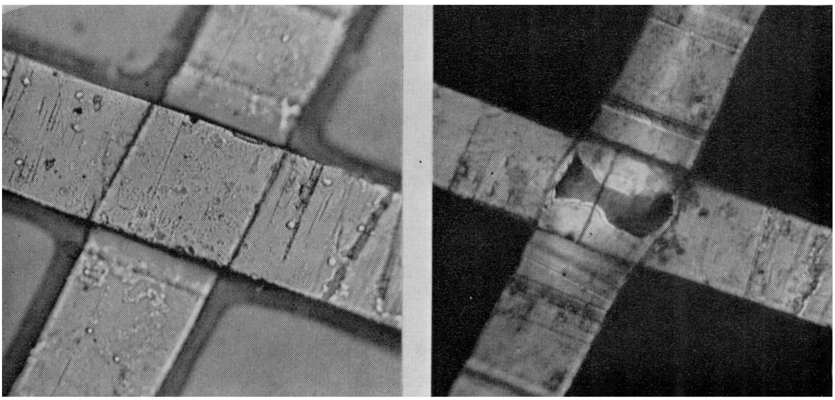
(a) (b) (c) (d)

Fig. 6—Frames from a ciné film of the drying and bonding of fibres

used for this experiment was soaked in water and allowed to shrink freely, upon redrying the 'machine'-direction displayed 15 per cent shrinkage compared with 6 per cent in the 'cross'-direction. The model fibres were cut so that their length axis corresponded to the machine-direction of the cellulose film, thus simulating the anisotropic shrinkage of pulp fibres.

To study bond formation, the model fibres were soaked in water for a few hours, then two of them were placed at rightangles in a drop of water on an inert surface (waxed paper) to which they would not adhere while drying. This is illustrated in Fig. 7*a*, in which water menisci between the fibres and the substrate are still apparent. After allowing the fibres to dry, the area of crossing was examined; using polarised vertical illumination, contact between the two fibres could often be observed, as in the case of natural fibres (micrograph Fig. 7*b* depicts it). This example displays to advantage the necking effect discussed above. The fibres have shrunk transversely, except in the region of the contact area, where the resistance to compression of the lower fibre has to a considerable degree prevented the shrinkage of the upper fibre.

This phenomenon could occur only if the process is indeed one of adhesion before drying and shrinkage: the experiment therefore substantiates the evidence of this phenomenon occurring in natural fibres.



(a) **(b)**

Fig. 7—A crossing between cellulose film fibres (*a*) wet, in vertical illumination, (*b*) dry and viewed with crossed polars to reveal the bonding

Effect of beating on the longitudinal compressional resistance of fibres

SHRINKAGE of paper increases with the degree of beating of the pulp. For instance, standard handsheets made from an unbeaten spruce sulphite wood pulp shrink a matter of 2 per cent when freely dried, whereas, after the pulp has been beaten for 60 min in a Valley beater, the shrinkage increases to 16 per cent. The authors' theory of shrinkage[1] explains this in terms of certain factors listed as controlling the amount of shrinkage. It has been shown that the intrinsic fibre shrinkage increases with beating and that the bonded area also increases. Little is known about the compressional resistance of the fibres, especially as the property that is really of importance is the resistance *during* the whole phase of the drying process and that at any time is acting against the immediate force of shrinkage of the crossing fibre.

Even so, an attempt was made to obtain some indirect assessment of how—or, indeed, whether—the compressional resistance of fibres changes with beating. The method adopted was to measure the amount by which a standard, cellulose fibre could shrink transversely at the bond site when bonding to the pulp fibres of interest. The standard fibre chosen was a hollow filament rayon, which collapses to a ribbon-like form. The method is more easily understood by reference to Fig. 8, which represents the crossing of two

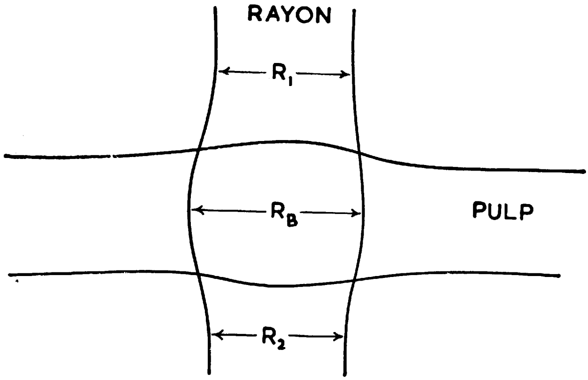


Fig. 8—Diagram showing the measurements made to determine the degree of necking at a bonded crossing between a pulp and a rayon fibre

fibres (dry)—one the rayon, the other the pulp fibre (this diagram does, in fact, illustrate the occurrence of the necking effect). From such a crossing, which was first of all confirmed in the microscope to have a high degree of bonding, the dimensions shown were measured. These were the widths of the rayon fibre R_1 and R_2 (measured just outside the region that was considered to be influenced by the bond site) and the width of the rayon fibre in the region of the bond R_B. In the case of crossings not at rightangles, these dimensions were measured in the direction parallel to the pulp fibre. Measurements were not taken from crossings where the fibres crossed at an angle of less than about 60°.

The most convenient way of obtaining a large number of such crossings was to make a very thin handsheet from a stock containing a 50/50 mixture of rayon fibres and pulp fibres. The sheets made had a substance of the order of 3 g/m^2 and, after the pressing stage, were allowed to dry on a surface that would not impede the natural shrinkage of the fibres. The sheets were then examined in the microscope and bonded crossings selected for measurement. The crossings were photographed on to 35 mm film and the measurements made by projection of the negative. The pulps used were a softwood, bleached sulphite (from a dry pulp lap), unbeaten and beaten for 10 and 60 min in the Valley beater.

The assessment of change in the longitudinal, compressional resistance of pulp fibres was based on the change that would be observed in the necking effect; if the compressional resistance were to decrease, say, with beating, then the necking effect would become less pronounced. The necking was determined from the difference between the dimensions R_1 and R_B or R_2 and R_B. In practice, the mean of R_1 and R_2 at each bond site was first calculated (designated R) and the difference between this and R_B was taken ($R_B - R$) as a measure of the necking. The value of this difference depends on, among other factors, the width of the fibre and so, to eliminate this variable, the difference was expressed as a percentage of the final width R. Hence, the parameter finally used to express the necking quantitatively was $N = (R_B - R)/R \times 100$ per cent.

The results, which are the mean values from the given number of measured crossings for the designated pulps, are given in Table 1.

TABLE 1—NECKING OF RAYON FIBRES WHEN BONDED TO BLEACHED SPRUCE SULPHITE PULP

Beating, min	*Number of crossings*	*Average value of N*	*Standard deviation of N*
0	15	9.9	6.9
10	23	8.7	5.3
60	30	11.25	6.7
60	18	11.7	7.0

It seems reasonable to suppose that the compressional resistance of pulp fibres is reduced by beating on the grounds that fibres become more flexible and swollen. If this is so and if the degree of necking is a measure of compressional resistance alone, then N should have decreased with beating. Owing to the high standard deviations, none of the average values is statistically significantly different; but, comparing the 0 and 10 min with the two 60 min beaten pulps, it should be noted that, if there is an effect of beating, it is opposite to that expected.

Such an effect could be explained in the following way. The degree of necking occurring at a bonded crossing depends not only on the longitudinal compressional resistance of the fibres, but also upon their intrinsic transverse shrinkage, as well as upon the extent and strength of the bonding throughout the drying and shrinkage phase. It has been shown elsewhere[3] that, with beating, the shrinkage of fibres increases and that the area of contact between fibres in a handsheet increases with beating.[5] Hence, it may be the case that, when bonded crossings are formed as in this experiment, the bonding has been enhanced with beating to an extent that is sufficient to override any decrease in longitudinal compressional resistance that may have occurred. If the bonding is stronger in some sense, then the compressional resistance offered by the fibres at a crossing can be transmitted more efficiently to act against the forces of shrinkage and is thus more effective in promoting the necking effect.

The corresponding values of the necking of the pulp fibres are given in Table 2. The value of N shown in this table now indicates the extent to which the pulp fibres have been restrained from shrinking at the bond site when bonding to the rayon fibres.

TABLE 2—NECKING OF PULP FIBRES BONDED TO THE RAYON FIBRES

Beating, min	*Number of crossings*	*Average value of N*	*Standard deviation of N*
0	15	6.2	4.8
10	23	6.2	7.8
60	30	13.0	10.5
60	18	16.3	13.0

The properties of the rayon fibres were constant with beating, as only the pulp fibres were treated. It can be seen that the necking of the pulp fibres increased with beating, which is the trend to be expected as a result of the increase in the free transverse shrinkage of the pulp fibres and perhaps, as discussed above, also the result of an increase with beating in the extent and/or strength of the bonding.

It should be appreciated from the above discussion that the final interpretation of this experiment still contains ambiguity in so far as three factors at the same time can control the extent of the parameter being measured and it seems impossible to separate two of these factors and measure their influence independently. However, what is established from the experiment is that not only does the necking effect exist, but it can be measured quantitatively. This is further vindication of the 'bonding before shrinkage' aspect of the shrinkage theory.

Examination of bond formation in paper at controlled moisture contents

To ENABLE a study to be carried out into the development of fibre-to-fibre bonds in the web while drying, the porous plate method[6] has been adopted for the removal of water from a wet web and bringing it to a known moisture content. A diagram of the arrangement used is given in Fig. 9. Essentially,

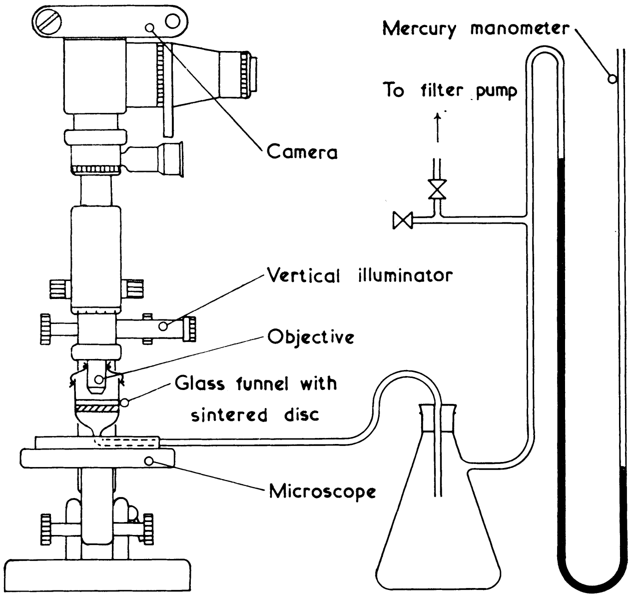


Fig. 9—The porous plate apparatus[6] as modified to follow bond formation in a drying web

the wet web was formed on a sintered glass disc contained in a funnel, which in turn was positioned on the stage of a microscope. The space under the porous plate was filled with water and to this a tension could be applied by means of a filter pump. The pressure was measured by a mercury manometer. The pulp stock used contained a large percentage of dyed fibres to facilitate observation of the bonding as previously described.[4] For the pulps used, a graph of moisture content against the applied tension is shown in Fig. 10. The web was formed *in situ* by filling the funnel with a fibre suspension of approximately 0.5 per cent consistency. Initially, the charge was drained rapidly by applying a large tension until the deposited mat had the form of a very wet web still possessing a layer of water above the surface fibres. The microscope objective was then lowered into position and the top of the funnel sealed to it by means of a sheath of plastic to prevent surface evaporation of the water from the web. A very small tension was applied and when equilibrium had been reached, which was found to take about 15 min, the surface was photographed by vertical illumination to record the condition of the water menisci and by polarised vertical illumination to record the bond-

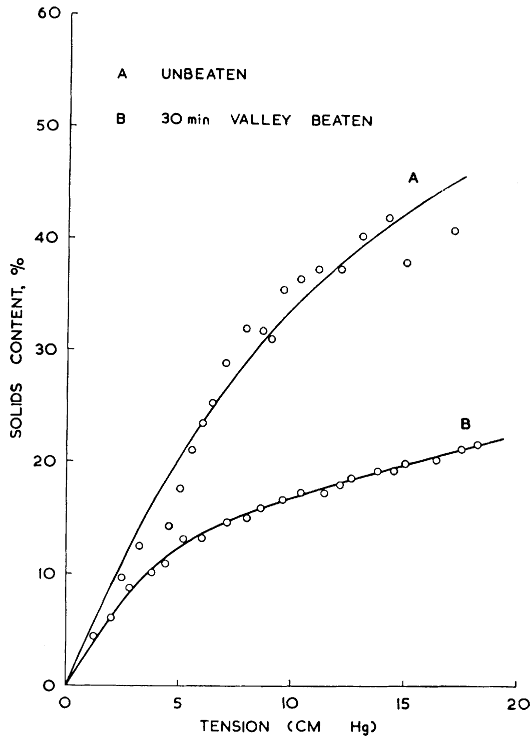


Fig. 10—Calibration curves for the pulps used in the porous plate apparatus

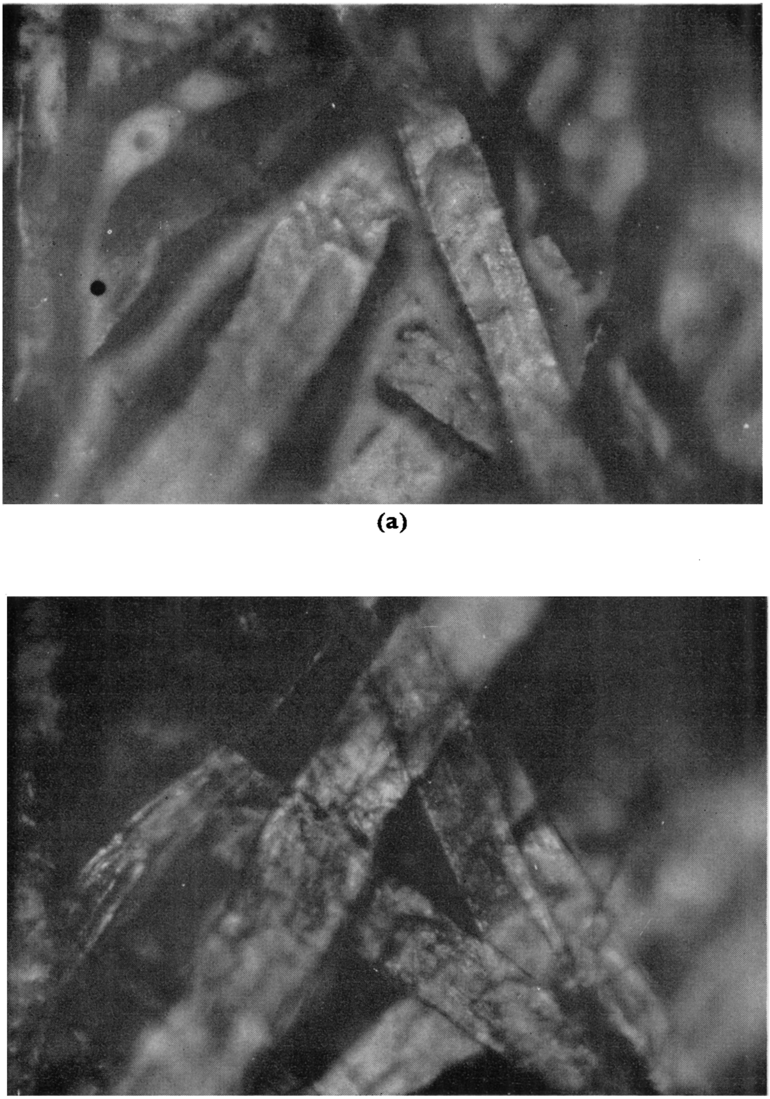
ing. This procedure was repeated while increasing the tension (thus removing moisture) in steps so that a record was obtained of the condition at various known moisture contents of the web. Finally, the web was allowed to come to the condition of air-dry, when the final state of the bonding was photographed.

Because space is limited, no more than two drying sequences can be illustrated by micrographs. In Fig. 11–14 is shown the drying sequence of an unbeaten, spruce sulphite pulp (from a dried lap). This is not typical in so far as no two sequences are exactly alike, but it does illustrate some of the features that are observed and the comments that follow are intended to be representative of observations made from many sequences of drying pads, using this sequence for general illustration.

The upper micrographs show the surface conditions and the lower ones show the fibres in polarised light ultimately to reveal the regions of bonding. The solids content at each stage are given in the figure captions. In the first figure (Fig. 11), the web has reached the stage at which the continuous layer of water that initially exists over the surface has receded to the point where the most prominent fibres begin to protrude from the surface. In the next picture, the water surface has receded further (in this region of solids content water appears to exist within the surface layer in the form of smaller menisci held at fibre crossings). Proceeding further, at the solids content corresponding to the third illustration, the small menisci contract and can no longer be seen. Often when comparing the appearance of the fibres in the region of this solids content with that when dry, they still have the appearance of being swollen and somewhat gel-like. The final air-dry state is illustrated in the last picture of the sequence (Fig. 14).

The development of the image under polarised illumination is shown in the lower pictures at the corresponding stages of solids content. In the final picture, the region of bonding (more precisely, contact) at the fibre crossing in the centre of the field can be seen as the black area. The degree of bonding at this crossing is about 75 per cent, one corner remaining unbonded; going back one stage, at 45 per cent solids content, a contact region similar to the final one can be observed, but with slightly more area in the form of a peninsula in the unbonded corner. Such slight losses in contact area have often been observed during the drying over this range of moisture content.

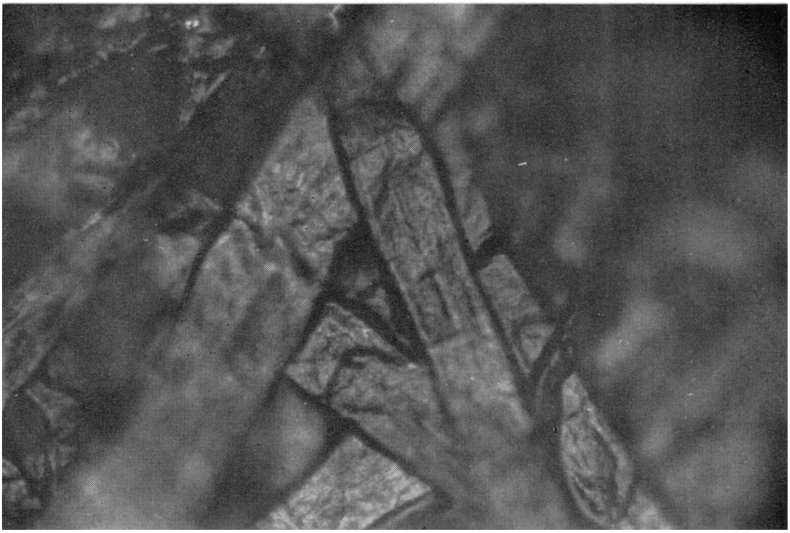
Two facts emerge from such observations. Firstly, it appears that for this unbeaten pulp the final regions of contact or bonding are beginning to form and can be observed in the region of a solids content of 45–50 per cent. (It is usual to observe them initially at a solids content very slightly higher than that in the illustration Fig. 13.) This is still at a moisture content when the fibres are saturated and swollen.[2] Secondly, some slight loss of contact area occurs during the final drying phase. This can be due to two causes. In the moist condition, there may exist, in the small capillary between the unbonded portion of the fibre crossing, a water meniscus giving the impression of bonded area that subsequently evaporates to give the appearance of loss of bonded area. Alternatively, the loss in contact area may truly be a breakage of bonded area caused by the shrinkage stresses of the fibres. In fact, it is believed that both phenomena have been observed. In the particular sequence illustrated, from the appearance, it is suggested that this is a loss of bonded area.



(a)

(b)

Fig. 11—Unbeaten pulp at 10 per cent solids content [×450]



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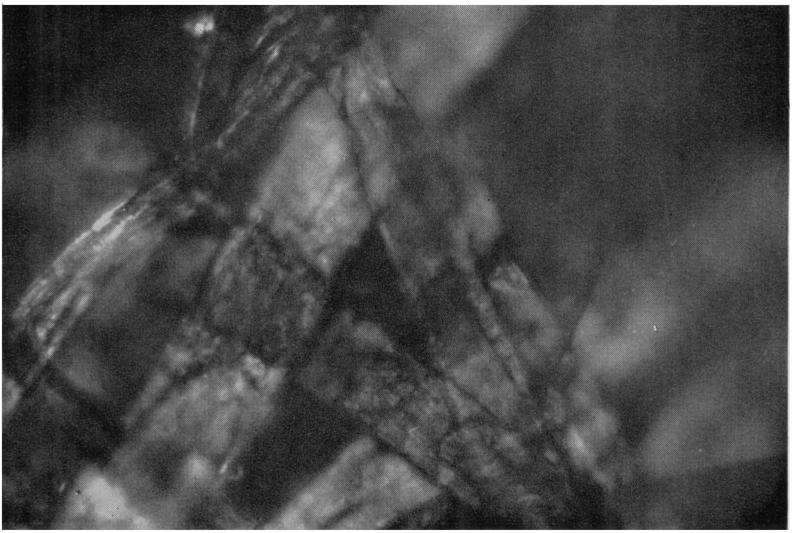
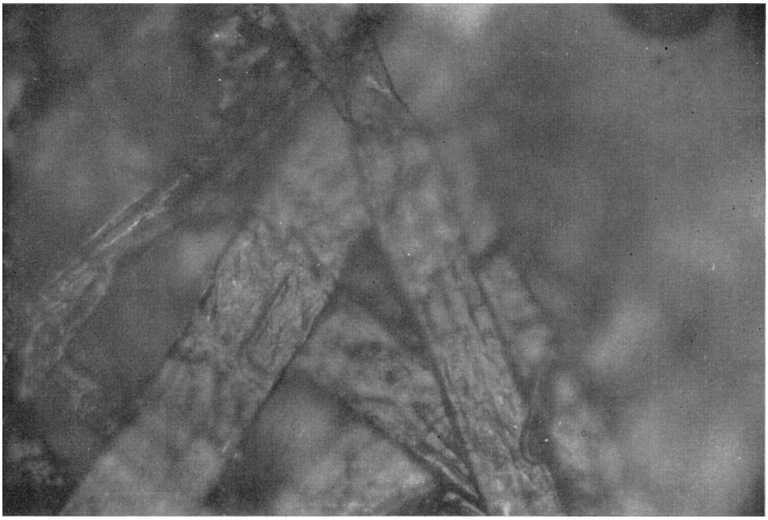


(b)

Fig. 12—Unbeaten pulp at 34 per cent solids content [×450]



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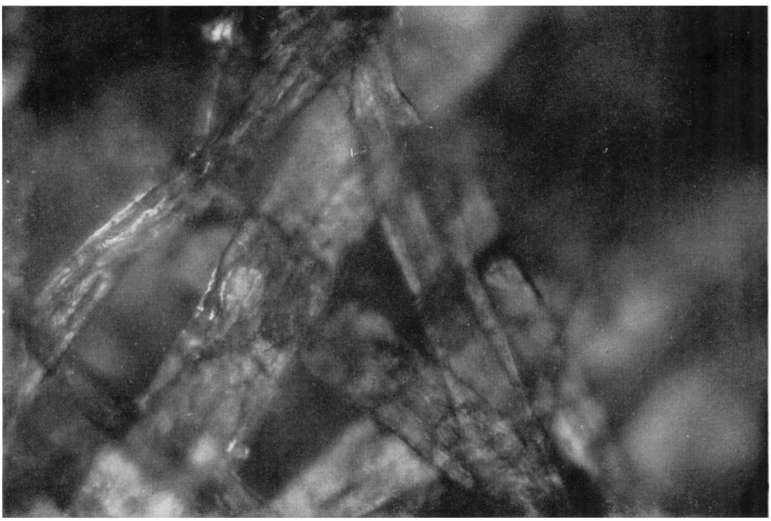

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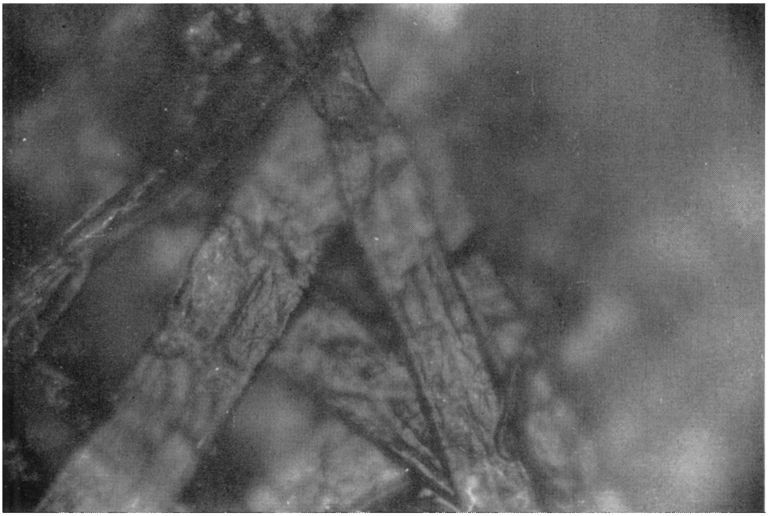
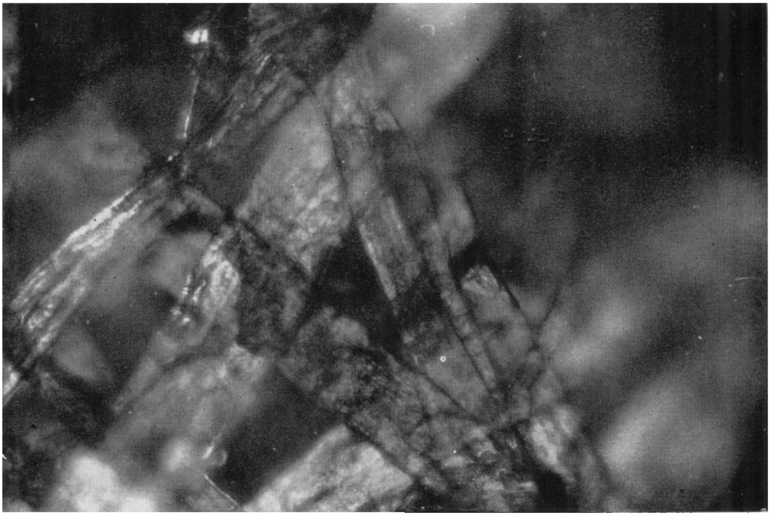
Fig. 13—Unbeaten pulp at 45 per cent solids content [×450]



(a)



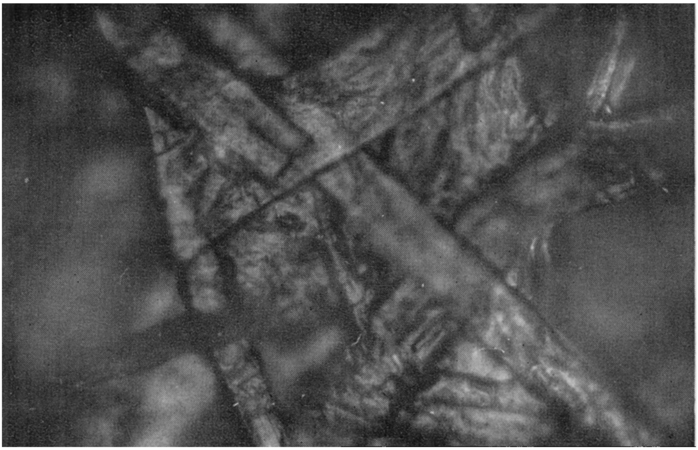
(b)

Fig. 14—Unbeaten pulp air-dried [×450]

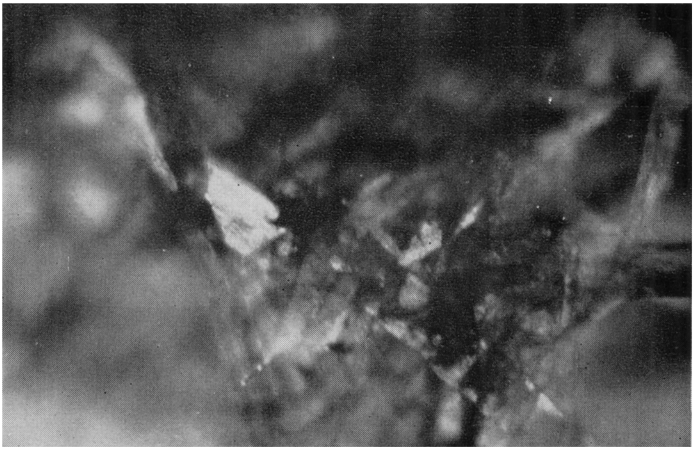
(a)

(b)

Fig. 15—Pulp beaten 30 min (Valley beater)—(*a*) at 10 per cent solids content, (*b*) at 12 per cent solids content [× 450]



(c)



(d)

Fig.15—Pulp beaten 30 min (valley beater)—(*c*) at 23 per cent solids content (*d*) air-dried [×450]

From observations of the recession of the water menisci, it is concluded that the surface layers begin to lose the continuous water at a solids content in the region of 10–15 per cent. If this is to be interpreted as the commencement of air intrusion into the web, it is in agreement with the stage at which Robertson[7] concludes it occurs.

A sequence, showing the appearance of only the water menisci during the drying of a pad of the same pulp beaten for 30 min in the Valley beater, is shown in Fig. 15 with the final bonding conditions in Fig. 15*d*. At 10 per cent solids content, the surface layer of water has just receded below the highest fibres; at 12 per cent solids, the water appears to be retained by menisci just below the uppermost layer of fibres. At 23 per cent, there is still some suggestion that water menisci are present below the top layer.

At this stage, work on the beaten pulp has not been concluded and, apart from the indication that entry of air into the pad occurs at a slightly higher solids content, no conclusions will be stated. It is intended to extend the range of solids content that can be covered in the apparatus by fitting a sintered disc of lower pore diameter, thus raising the tension limit imposed by the onset of air being sucked into the apparatus through the capillaries of the disc.

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Transcription of Discussion

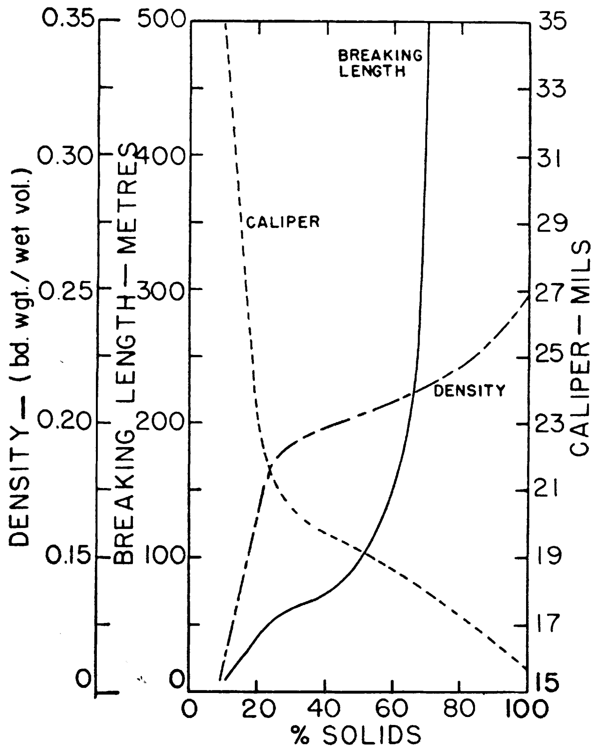
Discussion

Dr W. Gallay—In 1954, at an international symposium held in Appleton, I presented the basic work of Lyne and myself on the mechanism of wet web strength. In addition to other results (which need not concern us now), we reached the conclusion that interfibre adhesion played an important role in the development of the wet web strength at solids contents upwards of about 25 per cent. At that meeting, some sharp criticism was directed at this conclusion on the basis that no interfibre bonding could take place until the stage of fibre saturation was reached—that is, about 70 per cent solids. I was careful to explain—and I consider it worthwhile repeating on this occasion—that the concept of interfibre adhesion differs markedly from that of solid bonding.

Two wet glue surfaces show a marked tackiness when placed in relatively loose contact and a solid bond is not obtained until a sufficient stage of dryness is reached. This sort of adhesion is a matter of everyday experience in a variety of systems. A very close analogy to cellulose fibres from the point of view of chemical constitution and dimensions is provided by starch. Native starch granules show no adhesion to one another when brought into contact and they pack closely on sedimentation from aqueous suspension. When the ordered surface is slightly disrupted by mechanical means, however, thus setting free hydrophilic groupings, the starch granules can easily be observed to stick to one another in the water and the sedimentation volume increases markedly as a result of the structure formed by the adhesion. There is no question here of a rigid bonding attained on drying, but rather of an interparticle adhesion in actual two-phase suspension in water.

In order to realise this tackiness (or degree of adhesion between two surfaces), we must satisfy two requirements and only two requirements. We must have free hydrophilic groupings and we must bring them within a reasonable distance from one another. This distance will obviously depend also on the length of the molecules or fibrils free to take part in the adhesion.

The available hydrophilic groupings on the surface of cellulose fibres, which are responsible for eventual hydrogen bonding, are not developed at late stages of consolidation, but are in the main available at the outset of the papermaking process. This leaves then the question of the distance separating the two surfaces. Although hydrogen bonding involves distances of only several Ångström units, it is apparent that the effect of tack is operative over considerably greater distances of separation through several layers of water molecules.



[Reproduced from Lyne, L. M. and Gallay, W., *Pulp & Paper Mag. Can.*, 1954, 55 (11), 133]

Fig. D—Relationship of strength to caliper and density with increased dryness of groundwood webs

It has been stated also that the effect of increasing wet web strength upwards of 25 per cent solids might be explained by greater frictional resistance to separation by tensile force. In this connection, see Fig. D, from which you will note that there is initially a steep decrease in caliper of the wet web under the influence of surface tension after air intrusion. There is then a marked change in slope at about 25 per cent solids. Following this, we then have a marked decrease of caliper that continues on through the remainder of the consolidation. I believe this to be strong evidence of an increasing degree of interfibre adhesion throughout this range. In addition, on this question of interfibre separation, we have the very instructive photomicrographs of Pye, Washburn & Buchanan, which appear to show a large degree of intimate contact between fibres even before the couch and this would be at solids contents of less than 20 per cent. A good deal of evidence was adduced by Robertson to show that bonding begins at 43–48 per cent dry solids content and this is in good agreement with the 45–50 per cent figure given by Page. This is a long way from the high solids content demanded by the Campbell effect. I would hope that others will continue research in this field of interfibre adhesion in the region of solids contents well below this range of 45–50 per cent of which both Page and Robertson have spoken.

I am very pleased that this strong further evidence by Page has come along toward proof that earlier interfibre adhesion is a reality.

I said earlier that the hydrophilic groupings are already in the main available at the outset of the papermaking process. There should then exist the potential for a degree of interfibre adhesion at the beginning of the wire section or even earlier. At this morning's session, Steenberg and his colleagues explained the origin and existence of a fibre network on a purely mechanical basis. According to this concept, the fibres in the network are locked into the structure by internal stresses. Each 'active' fibre presses against several others with a force sufficient that the whole assembly has the properties of a viscoelastic body.

On interfibre adhesion, a very pertinent question must be asked—when two surfaces touch, how far apart are they? It is apparent that, under the stresses involved, nearly all of the water between the fibres at crossover points has been pushed out of the way. It seems reasonable to suggest that the remaining few layers of water molecules that separate the fibre surfaces are held there by forces greater than the stresses tending to spring the fibre back to the form of least energy.

This brings us to an area in cellulose/water relationships that needs further development. There is a great deal of incontrovertible evidence that the first layer of adsorbed water is held by the cellulose surface with a very high level of energy. There is also ample evidence to show that this level of energy decays with succeeding layers of sorbed water until the water take-up is thermodynamically neutral. I would regard the swollen fibre (in so far as this merely occluded water is concerned) as a sponge on the molecular level and I am not surprised that Van den Akker was able to squeeze water out of a fibre down to relatively high solids content using reasonable pressures.

Where we require more precise information, however, is in the area of the heats of sorption or other thermodynamic data about the few layers of water molecules adsorbed after the first layer. This would enable us to deal with the magnitude and extent of longer range attraction and the accompanying role of overlapping spheres of influence of water layers between two fibre surfaces. On this basis, it would be unwarranted to assume that interfibre adhesion plays no part in the mechanism of network structure.

Mr D. H. Page—What has not come out too clearly from this paper and from our paper on the shrinkage of fibres is their interconnection. We did not do these two pieces of work independently: we hoped that our work on the moisture content/shrinkage curve of fibres would shed light on the moisture content/shrinkage curve of paper. The point about our work on the transverse shrinkage of fibres is that the moisture content of fibres when they began to shrink was found to be very high compared with those earlier ideas that Gallay was mentioning.

In that work of transverse shrinkage, there was no quantity of water outside the fibre: it was all contained in the fibre wall and very high values were obtained—in one case, as high as 100 per cent.

Chairman—Were the films of the fibres dancing after or during shrinkage time sequences?

Mr P. A. Tydeman—Yes, they were time sequences. I merely wanted to record the qualitative effects in the film. The fibres were being dried on a gridwire and the photographs taken by ciné camera using time lapse. Roughly speaking, one frame was taken every 5 sec during the natural drying of the fibres under the microscope and the film was shown at 16 frames/sec. The drying would take (depending upon the specimen and how much water was retained when put on the gridwire) anything from 5 to 15 min.