Preferred citation: D.H. Page and J.W. Sargent. The fine structure of fibre bonding. In **The Formation and Structure of Paper**, *Trans. of the IInd Fund. Res. Symp. Oxford, 1961*, (F. Bolam, ed.), pp 195–200, FRC, Manchester, 2018. DOI: 10.15376/frc.1961.1.195.

THE FINE STRUCTURE OF FIBRE BONDING

D. H. PAGE AND J. W. SARGENT

BRITISH PAPER AND BOARD INDUSTRY RESEARCH ASSOCIATION, KENLEY

In earlier papers,[1,2] the possibility of the use of light microscopic methods for the observation of optical contact regions between fibres in paper sheets was described and arguments were put forward that these areas of contact define the regions within which strong adhesive forces operate. While sufficient confidence in this view was held to use the technique for studies relating to geometry of fibre-to-fibre bonding in paper, it was considered that the question of the fine structure within these contact regions was sufficiently important to warrant a separate investigation, the initial results of which are given here.

It must first be emphasised that these areas of contact between fibres are almost invariably very well defined in the light microscope and show a sharp contrast in intensity between them and the remainder of the fibres. Theoretically, it is possible to obtain a measurement of the distance separating two fibres from measures of the intensity of light coming from the contact zone and from the first bright interference fringe around it. Such measurements are prone to large errors, owing to the optical heterogeneity of the fibre through which the observation is made and to the scattering of light, both at the surface of the fibre and in the fibres beneath, which may not be completely eliminated by the optical technique employed. These errors would always give an overestimate of the separation.

Under the most advantageous conditions for observation—namely, with two early wood fibres—the intensities observed correspond to a separation in the region of 150 Å. In view of the microfibrillar roughness of each surface and the extent over which these surfaces are in such close contact, it seems likely that a vast number of opportunities for bonding will occur and that bonding sites are well distributed over the whole of these areas.

It is surprising that such large areas of close contact exist between fibres, since their natural form is much rougher than is suggested by this separation.

(Presented by Mr. D. H. Page as part of the delivery text of the previous paper by Page, Tydeman and Hunt)

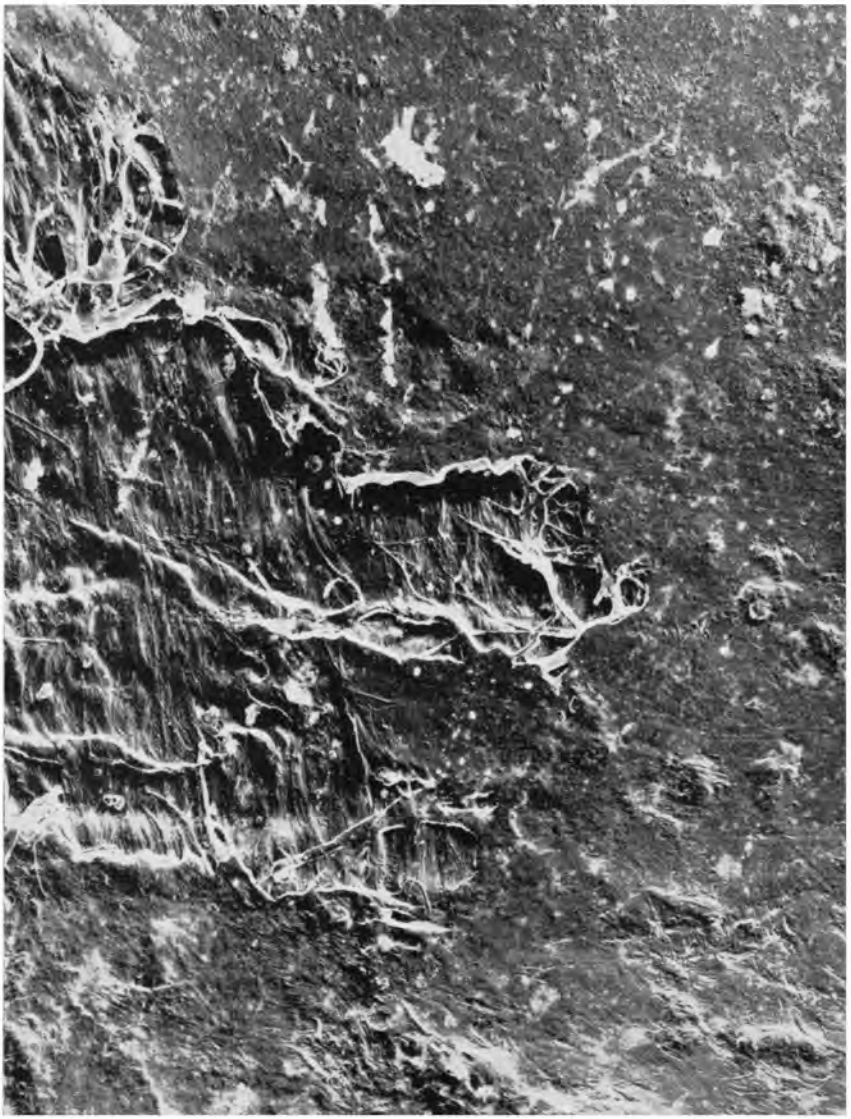

Fig. 1—Machine-glazed paper: the contact between the fibre and the metal has been close enough for the structure of the metal to be reproduced on the fibre even on this fine scale—carbon replica[7,8,9] (× 6 000)

Fig. 2—Handsheet of unbeaten spruce sulphite, showing areas in which the fibre was glazed to the drying disc: note the sharp discontinuity between glazed and unglazed areas, in particular the 'cliff' at lower left—carbon replica (× 4 500)

It is evident that the regions of optical contact observed are in fact regions in which the forces of wet pressure and surface tension have caused a collapse of one fibre on to the other.

So far, the only published work on the fine structure of fibre-to-fibre contact zones is that of Asunmaa and Steenberg[3] and of Jayme and Hunger.[4,5] The former authors studied ultra-thin sections by electron microscopy, whereas the latter used replica methods on fibre-to-fibre contact zones that had been mechanically separated. In view of the need to correlate the results of light microscopy with those of electron microscopy, it was decided to adopt a procedure that was basically different from those given above. Instead of examining fibre-to-fibre bonds, an examination was made both by light microscopy and electron microscopy of the same areas of the bonds that form when fibres dry on to a standard substrate. Additionally, this procedure enabled the closeness of contact between the fibre and the substrate to be estimated by determining the extent to which the fibre surface adopted the structural appearance of the substrate.

An example of this latter effect is shown in an electron micrograph of machine-glazed paper (Fig. 1). The structure of the MG cylinder has been perfectly reproduced by the paper, even on a submicrofibrillar scale and a sharp discontinuity is apparent between the glazed and unglazed areas. This effect is not due solely to the heat and pressure applied during machine-glazing, since it can be observed also on standard handsheets plate-dried at room temperature (Fig. 2) and it seems likely that a closeness of contact similar to this can exist between fibres. Furthermore, two fibres both of which are plastic will tend to give even closer contact than that produced between a fibre and a rigid surface.

It should be noted that these electron micrographs (Fig. 1 and 2) do not exhibit the raising of microfibrils in the areas of contact to the extent shown by Jayme and Hunger.[4,5] This is not interpreted as precluding the existence of adhesive forces between the fibre and the metal, since it is clear that extremely close contact has been achieved; moreover, it is an experimental observation that considerable forces are required to remove the handsheet from the metal. It seems likely that in the regions of contact the cohesive forces holding the microfibrils together are generally greater than the forces of adhesion between the microfibrils and the metal.

In the case of paper glazed to glass, which has many available bonding sites, the lifting of microfibrils in the regions of contact is generally observed (Fig. 3). It is not considered that those microfibrils that lift are the only ones taking part in the adhesion process, but rather that the adhesion of these microfibrils to the glazing surface was greater than their cohesion to the

parent fibre. Once again, the sharp delineation of the region of contact is observed.

A number of observations of optical contact have been made in the light microscope between paper and glass to which it has been glazed and the exact regions of contact have been photographed in the electron microscope. The general principle holds that the optical contact regions can be clearly recognised in the electron microscope as an area in which adhesive forces have operated, but a consideration of the structures within these areas will form part of a later publication.

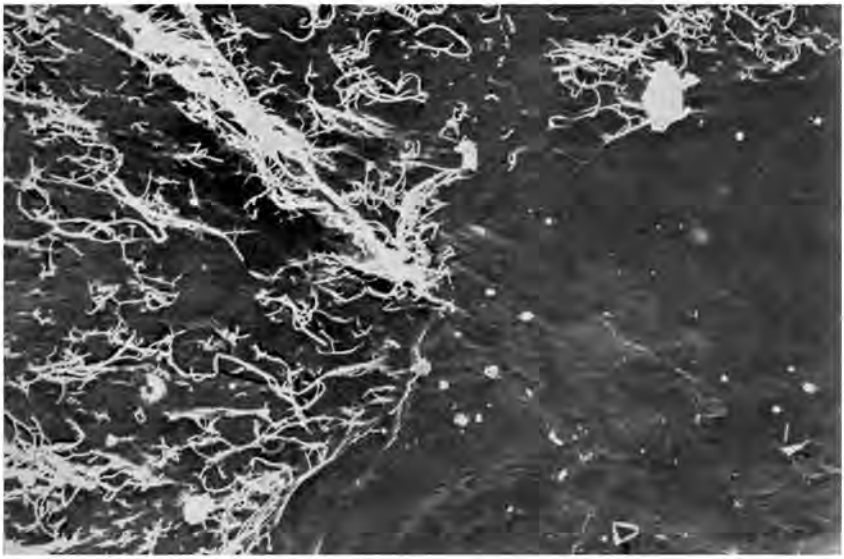

Fig. 3—Fibre glazed to glass showing sharp boundary of raised microfibrils—carbon replica (× 6 000)

The effect of the natural surface topography of fibres on their ability to form large areas of close contact has been recognised.[2] The gross topography (which is due to the mode of collapse of the fibre during drying) can have a considerable effect on the extent of the areas of contact, but this effect is reduced by beating,[6] apparently because of the increased plasticity of the fibres. The finer structure, in particular the wrinkles caused by drying and the anatomical features of the fibre, has less effect and indeed, after beating, the fibre wall is sufficiently plastic for their effect to become negligible. An example of this is seen in Fig. 4: the wrinkles on the fibre do not extend into the contact zone.

It has been shown that these areas of collapse of one fibre on to another, seen in the light microscope as areas of optical contact and in the electron microscope as areas of adhesion, because of their size and frequency of occurrence, are of prime importance in governing the properties of paper. While it is considered that fibrillated material spanning from one fibre to another outside the regions of contact will have great importance for some

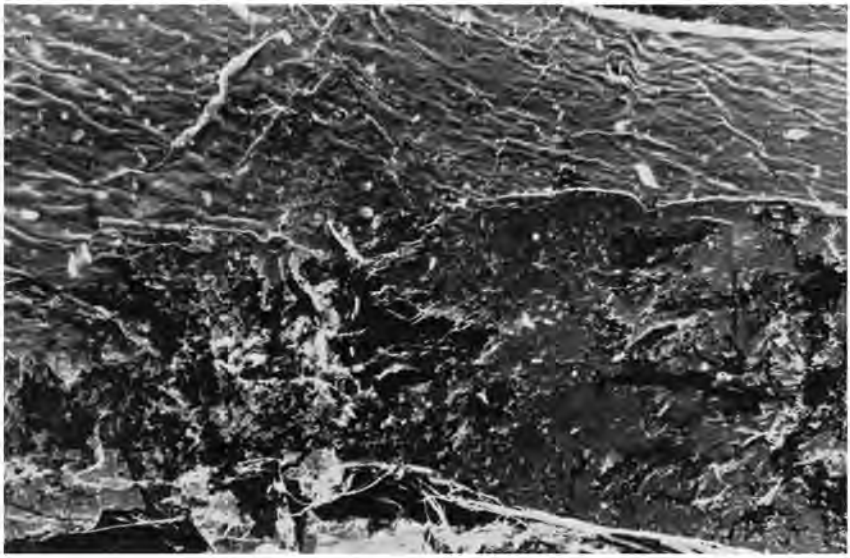

Fig. 4—Fibre glazed to glass showing smoothness of contact region—carbon replica (× 3 000)

properties (for example, porosity), it is thought to be of secondary significance in determining the strength properties of most papers.

REFERENCES

1. Page, D. H., *Paper Tech.*, 1960, **1** (4), 407–411
2. Page, D. H. and Tydeman, P. A., *Paper Tech.*, 1960, **1** (5), 519–530
3. Asunmaa, S. and Steenberg, B., *Svensk Papperstidn.*, 1958, **61** (18b), 686–695
4. Jayme, G. and Hunger, G., *Wochbl. Papierfabr.*, 1957, **85** (23), 900–901
5. Jayme, G. and Hunger, G., this vol., 135
6. Page, D. H., Tydeman, P. A. and Hunt, M., this vol., 171
7. Bradley, D. E., *Brit. J. appl. Phys.*, 1954, **5**, 65–66
8. Comer, J. J., Stetson, H. W. and Lyons, S. C., *Tappi*, 1955, **38** (10), 620–624
9. Jayme, G. and Hunger, G., *Mh. Chemie*, 1956, **87** (1), 8–23

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.