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SOME EXPERIMENTAL OBSERVATIONS WITH A BEARING ON THE PAPER 'A NEW THEORY OF THE SHRINKAGE, STRUCTURE AND PROPERTIES OF PAPER' BY D. H. PAGE AND P. A. TYDEMAN

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AT the suggestion of Page and Tydeman, we have examined the structure of freely dried handsheets, using the scanning electron microscope. This was done because of the unique advantages of this instrument for this type of examination and in the hope that an independent test of their theory could be made.

In the present work, unbleached kraft pulp was beaten to 450 CSF and 60 g/m^2 handsheets were formed in a British sheetmachine under standard conditions. The sheets were pressed at 50 lb/in^2 between plates and blotters. After pressing, one sheet was dried on its plate with the usual restraining ring in place. A second sheet was peeled from the plate, floated on mercury so that it was free to shrink and air dried at room temperature.

The surfaces of these two sheets were then examined in the scanning electron microscope, using the technique described elsewhere at this symposium (pp. 101–108). The method of examination was to choose several fields at random and take low magnification pictures of these. In each of these low magnification fields, several rightangle fibre crossings were selected and photographed at higher magnification. These were then used to estimate the extent of compression in fibres over bonded areas.

Visual examination of the pictures gave the following results. Three independent observers agreed that 12 out of 16 fibre crossings in the freely dried handsheet exhibited microcompressions compared with only 3 out of 12 in the plate-dried handsheet. In addition, the severity of the compressions was obviously greater in the former. For both handsheets, doubtful cases were listed as having no compressions.

In this short note, it is impossible to illustrate completely the extent and variety of the microcompressions observed. Only eight pictures of the freely dried handsheet have been chosen to illustrate some of the results (Fig. 1–8). Fig. 1 is a low magnification picture of a randomly chosen area and Fig. 2, 3

This work was carried out subsequent to the presentation of Page's work at Oxford at the suggestion of the authors Page and Tydeman: the text of this contribution was received 11th December 1961

and 4 are examples of rightangle fibre crossings within this area. In these examples, the compressions occur more strongly near the edges of the bonded areas.

Fig. 5 is another low magnification field in the freely dried specimen. Fig. 6 and 7 are higher magnification pictures of bonded areas of a fibre that runs from the top left to the bottom right in the field of Fig. 5. Fig. 6 shows a fibre crossing exhibiting the least evidence of microcompressions of any observed in the freely dried sheet. In Fig. 7, microcompressions are evident where the uppermost fibre contacts the broad lowest fibre, but are absent where the top fibre contacts the middle fibre.

Fig. 8 illustrates an allied effect that has been observed in this study—the effect of compressive forces causing a fibre to kink and fold beneath another fibre that it is crossing.

In conclusion, a microscopic examination of the surface of paper supports the theory of Page and Tydeman that the shrinkage of freely dried sheets is partially accommodated by the longitudinal shortening of fibres at the bond crossings as shown by microcompressive failures at these sites. It should be noted, however, that these pictures are all of fibre crossings on the surface of a handsheet and they do not give evidence of how bonded areas accommodate shrinkage in the centre of the sheet, where the geometry is more complicated.

Fig. 1

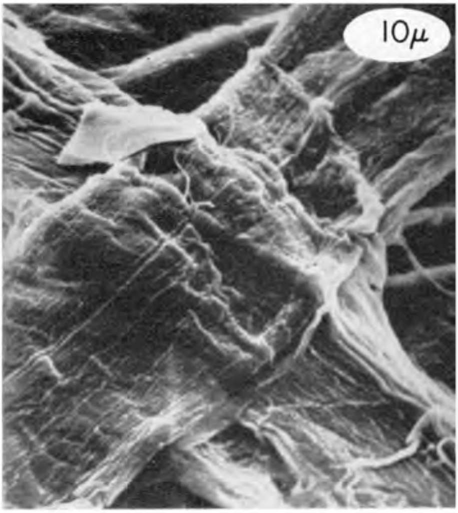

Fig. 2

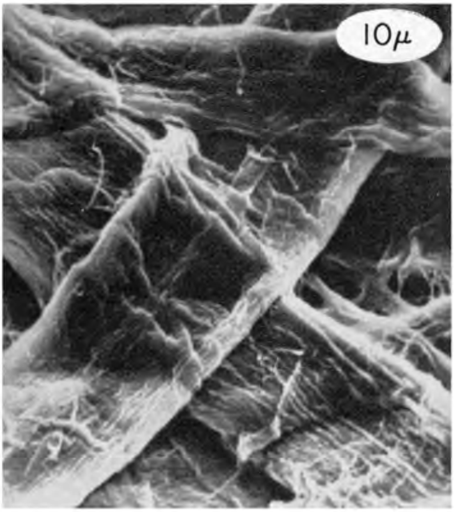

Fig. 3

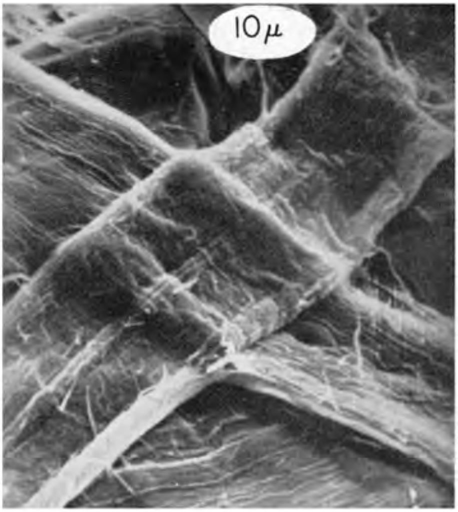

Fig. 4

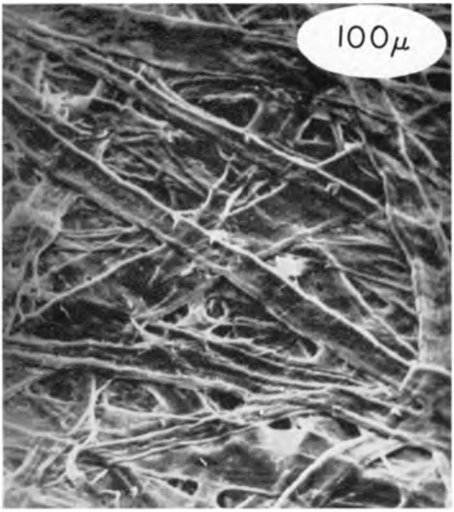

Fig. 5

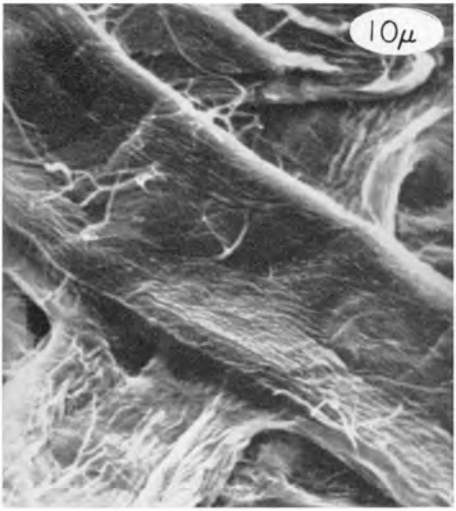

Fig. 6

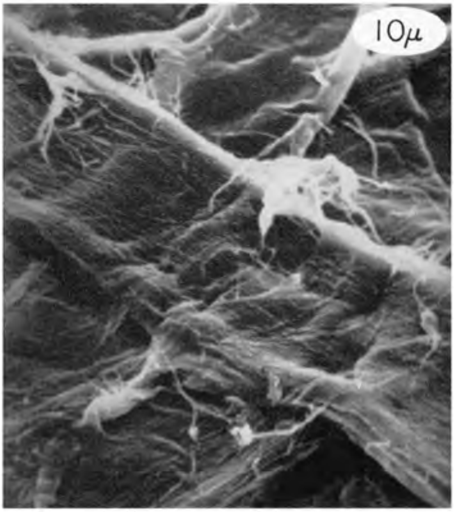

Fig. 7

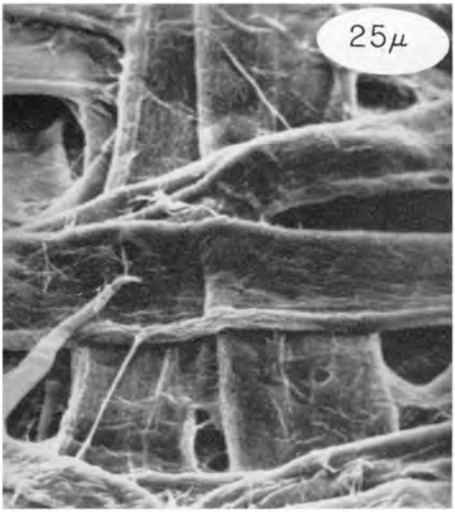

Fig. 8

Transcription of Discussion

DISCUSSION

MR. R. R. COUPE: My first point concerning the penetration of non-interacting liquids is that there is a fundamental difference between the flow of liquid into a single capillary tube and that into a porous structure like paper. As liquid rises, the whole of the tube below the meniscus is filled; but with paper there are always air spaces below the height to which some liquid has risen. It can be shown experimentally that the liquid held on the strip is distributed in the way shown in Fig. D12.

In practice, most interest centres round the penetration in a direction at rightangles to the plane of the sheet, but the same considerations must apply. The shape of the penetration function would be similar and the kinetics can

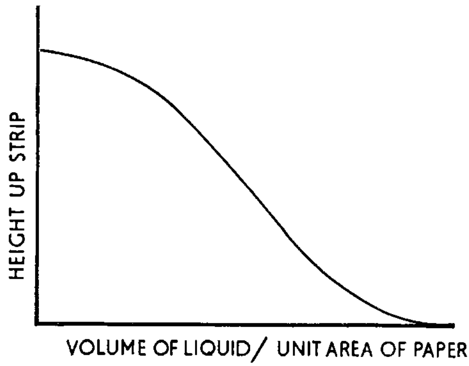

Fig. D12

probably be formulated in a similar way, with the introduction of appropriate shape factors.

My second point concerns the fact that, when liquid is penetrating paper under practical conditions, there is no large reservoir of liquid. In fact, the amount of liquid available may be small in relation to the pore volume of the sheet and this has a very significant effect on the fundamentals of penetration. The depth to which liquid penetrates under a given pressure (200–1 000 lb/in^2 range) and time (several centiseconds) is related to the thickness of liquid film available (range up to 25 microns) by a function shown in Fig. D13.

The actual curve depends upon the structure of the sheet in question—for example, a maximum penetration is not reached at any thickness up to

25 microns (maximum experimental limit) with an open-structured antique paper.

Using the techniques developed at PATRA,[1] it has been possible to study the dependence of distance of penetration on the variables of pressure, time and viscosity. The relationship found experimentally is—

$$h = C\left(\frac{pt}{\eta}\right)^{1/2}$$

where c is a constant.

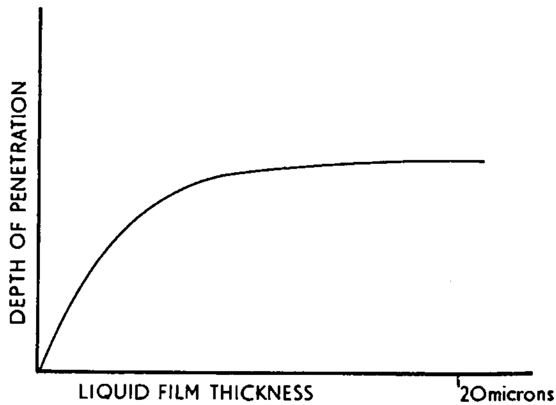

Fig. D13

This is the same form of expression that can be derived by integration from the Darcy equation—

$$\frac{dl}{dt} = K\frac{P}{\eta l}$$

This agreement with classical theory is very satisfactory, until one remembers that Darcy's law was derived and has been verified from the flow of liquids through compacted beds of incompressible substances like sand, cement and pigments.

I am not suggesting that these results show that paper is an incompressible network, for clearly it is not, but that they are throwing some interesting light on the influence of structure and compressibility on fluid flow.

[1] Coupe, R. R. and Hsu, Baysung, *Appl. Sci. Res.* (Section A), 1961, **10** (3–4), 253–264

DR. E. BACK: In respect to the water resistance of sized papers, there are important limitations in the equations (*10*), (*11*) and (*12*) because of the contact angle. According to electron microscope work, the aluminium soaps formed in paper sizing appear as discrete hydrophobic particles on the hydrophilic cellulose. The approach of Phillippoff[2] to the mean contact angle of heterogeneous surfaces must be considered.

For the effect of surface roughness on contact angles, I would like to draw attention to fundamental measurements of Bartell and Shephard.[3]

Actually, we measure an apparent static contact angle of water as high as 120°–130° on sized papers. In spite of this, the water penetrates.

In dimensional stability, the two main independent parameters are the equilibrium dimensional range (EDR) and the permanent dimensional change (PDC), obtained separately after cycling the paper repeatedly between two predetermined relative humidities.* In wet expansion, both these parameters are involved. The PDC is mainly dependent on drying stresses in the paper; the EDR is mainly determined by the fibre and stock properties. With a given papermaking stock, the only efficient way to reduce the EDR is to transform hydrogen bonds into covalent bonds, for example by heat treatment in the presence of a catalyst. This can be done to some extent and, because this bond transformation (dehydration) in heat treatment takes place in a fairly water-free state, the paper compared to a given relative humidity has shrunk. Thus, the PDC of this paper is low or even negligible.

MR. J. MARDON: I wish to present a written contribution from Prof. Scheidegger on flow through porous media. The subject matter of his contribution is quite important to us all in the paper industry. We tend to accept uncritically the Kozeny-Carman equation, which is almost completely suspect in the way we very often use it: in fact, it is numerically reliable only within a factor of ten.

DR. H. CORTE: I would like to stress the conceptual difficulties in defining geometrically what could be called a *pore* in a three-dimensional network of fibres. Such a definition not existing, we find the only way out is in a physical definition. This means that it depends on the experiment what a pore is.

MR. J. F. T. HARRIS: From the paper by Baird and Trubesky(7) are quoted figures for the apparent density and void volumes for normal papers. I wish to extend these figures to include filter paper.

[2] Phillippoff, W., Cooke, S. K. and Cadwell, D. E., *Mining Eng.*, 1952, **4** (3), 283–286
[3] Bartell, F. E. and Shephard, J. W., *J. Phys. Chem.*, 1953, **57** (2), 211–215; (4), 455–458
* This has been pointed out by Hudson, Rance *et al.*

There are a number of commercially produced filter papers with apparent densities as low as 0·14 and with void volumes of over 90 per cent. In this type of paper, the proportion of the voids that exist as real pores is 90–95 per cent of the total void volume. This contrasts with the proportion of 1–2 per cent found by Baird in other types of paper.

DR. R. P. WHITNEY: I should like to point out that the Kozeny-Carman relation is still being applied extensively to flow through porous fibrous media such as paper, because it is still the best relation available. If the equation is used properly, with due regard to its limitation—for example, proper evaluation of the so-called Kozeny constant, which is not a constant at all—it will yield results far more reliable than the tenfold that Scheidegger mentions.

THE CHAIRMAN: I remember that, when I first started research work on permeability, the literature was full of criticisms of the Kozeny equation. The criticisms are just the same, but the equations are being used as effectively today as then. Kozeny's constant k is an empirical coefficient and people should really be careful how they use it.

MR. P. E. WRIST: Scheidegger's justifiable criticism of the Kozeny-Carman concept has given rise to the impression that, until such time as someone works out a statistical theory to replace it, we are left with nothing reliable to use in its place. I think that is not quite true. In fact, without many people realising it, Davies and Ingmanson have put forward an adequate empirical relationship in its place. The Kozeny-Carman concept is based on a capillary model, one in which the media is treated as a system of capillaries.

It was a concept put forward to relate the constant of proportionality in the Darcy equation to the porosity of the media and contains a 'constant' of its own that was to be independent of porosity. Within a narrow range of porosities, this is in fact almost true, hence the limited successes of the concept. At high porosities, however, the Kozeny-Carman 'constant' becomes a function of porosity, hence the criticism. More recently, Davies, working with gaseous flow through textile fibre beds and Ingmanson, working with water flow through beds of synthetic fibres of papermaking dimensions, have derived very similar empirical relationships correlating the Darcy constant with the mat porosity. A recent theoretical study of flow through parallel arrays of cylinders by Happel lends theoretical support to the Davies-Ingmanson equations. Fig. D14, taken from a forthcoming paper by Meyer,[4] shows that

[4] Meyer, H., *Tappi*, 1962, **45** (4), 296-310

the theoretical curves of Happel for the dimensionless Darcy constant for flow perpendicular to and parallel to cylindrical arrays envelope the Davies-Ingmanson curves. At high porosities, the empirical curves fall midway between the two, as might be expected from a random array of the fibres. As the porosity decreases, the curves approach the curve for flow across the cylindrical array.

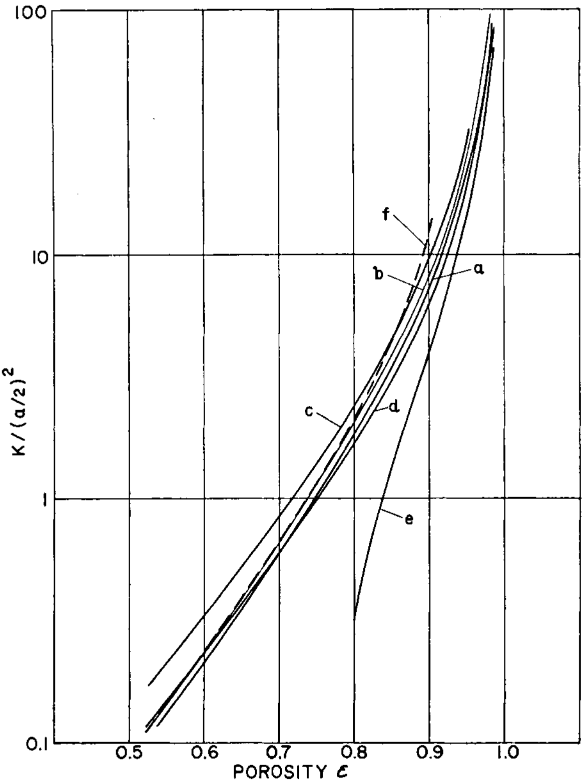

Fig. D14—Darcy constant as function of porosity ϵ

Curve *a*: after Davies: equation (*4.2*)
Curve *b*: after Ingmanson: equation (*4.2*)
Curve *c*: after Happel: parallel, equation (*4.3*)
Curve *d*: after Happel: perpendicular, equation (*4.4*)
Curve *e*: after Hasimotu: perpendicular, equation (*4.5*)
Curve *f*: after Kozeny-Carman: equation (*4.1*)

(From *Tappi*, 1962, **45** (4), 300)

I suggest that, until such time that a more rigorous treatment is available, the empirical equation of Davies-Ingmanson, which is not based on a model at all, but in fact approximates results based on a 'fluid drag passed cylinders model', is a very satisfactory basis for a study of flow of fluids through fibrous mats such as paper. The appropriate references are contained in my paper to be presented on Friday.

PROF. W. BRECHT: This discussion shows that the subject dealt with presents complicated problems. One of them is the question whether the equation established by Kozeny and Carman can be applied to determine the permeability of fibrous media. Scheidegger[5] in his excellent book criticises this equation very carefully, indeed. Unfortunately, I could get it only after my paper was finished.

[5] Scheidegger, A. E., *The Physics of Flow through Porous Media* (University of Toronto Press, 1960)