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SCANNING ELECTRON MICROSCOPE STUDIES OF SPREADING OF LIQUIDS ON PAPER

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Synopsis The important roles of sheet roughness and porosity and of fibre morphology on the way liquids spread on paper are revealed by static and dynamic scanning electron microscopy. Some preliminary results are described that demonstrate the potential value of the technique.

Introduction

THE ways by which a liquid wets and spreads on the surface and into the substrate of paper are often important when paper is processed or used. Quantitative equations describing the phenomena, such as the classical Young equation for the equilibrium contact angle θ, are usually derived from theories assuming that the surface is homogeneous and geometrically smooth. The importance of surface roughness and heterogeneity is recognised, but their effects have not been adequately taken into account.

In this brief note, we describe the use of the scanning electron microscope (SEM) in studying stationary and moving liquid drops on paper surfaces and we demonstrate how important surface roughness can be. Since the structure of paper is so complicated (and because of limitations of the SEM), these studies thus far are merely qualitative. We are also making quantitative studies by other techniques and with a variety of model rough surfaces having well-defined surface topography.(1, 2) Of particular theoretical importance are sharp edges on solid surfaces: these act as barriers to the spreading of a liquid(1) as illustrated in Fig. 1 & 2 by the elongation of a drop on a grooved surface. As will be seen later, this inhibition of spreading exists at fibre and sub-fibre levels in paper.

Stationary drops on paper

IN THE preliminary work on paper, we allowed molten drops of polythene (PE) and polymethylmethacrylate (PMMA) to spread and solidify on a paper

Under the chairmanship of Prof. M. F. Judt surface. The samples were then mounted on an aluminium specimen stub and metallised with 300 Å thick gold-palladium alloy to render the surfaces electrically conducting and observed in the SEM (Cambridge Instruments, Stereoscan 2A). Fig. 3 & 4 obtained in this way illustrate the profound effect of surface roughness and porosity on the wetting behaviour, also the obvious difference between the macroscopic contact angle normally measured and its microscopic value, which can vary from point to point. This technique was later replaced in preference for the one described below because of possible complications from solidification of the polymer, especially the contraction in volume.

A more satisfactory technique (also used in the dynamic experiments) employs drops of polyphenylether (PPE) vacuum pump oil (Santovac 5, Monsanto Chemicals), which can be observed directly in the SEM. PPE has a viscosity (25° C) 22 P, and surface tension (25° C) 43 dynes/cm and is very involatile. The disadvantages of the method are that (*1*) the paper surfaces must be metallised thereby changing the surface free energy and (*2*) the liquid can accumulate electrons that may produce artefacts in the SEM images and, for these reasons, the observations are qualitative.

Fig. 5–8 shows the resulting behaviour of the contact line of the liquid and profile of deposited PPE liquid drops on glassine papers. The smooth surface of the supertransparent glassine paper (Fig. 5) is quite evident and the contact line has little irregularity; there are some imperfections in the sheet, however, which serve as local capillary channels. At a higher magnification (Fig. 6), the contact line appears wavy, but both the amplitude and wavelength are small. Similarly, the contact angle θ does not appear to vary significantly along the contact line: the macroscopic $\theta = 28°$ (measured at low magnification) is almost the same as the microscopic values (measured at high magnification).

On the other hand, for the opaque glassine, which during manufacture was subjected to less supercalendering and contains inorganic pigment, the contact line appears less regular because of the increased surface roughness (Fig. 7) and yields a macroscopic $\theta = 20°$. At higher magnification (Fig. 8), the contact line is seen to be quite ragged, causing local changes in the drop profile. Wherever the contact line protrudes, $\theta < 20°$ and can be zero; whereas, in regions between the protrusions, θ is greater.

A cast-coated paper appears to provide a smooth surface, since almost symmetrical spreading of the liquid drop has resulted (Fig. 9). The shadow-like band surrounding the circular drop, however, is undoubtedly due to the porosity of the coating (Fig. 9). Thus, absorption and spreading of the liquid occur simultaneously; the width of the absorbed band of liquid indicates the importance of this on the spreading of the drop. Local surface heterogeneities

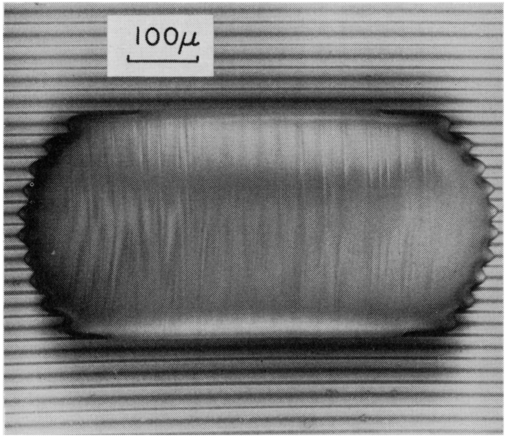

Fig. 1—SEM graph of polyphenylether (PPE) liquid drop on a model grooved nitrocellulose surface similar to a high fidelity gramophone record viewed from the top

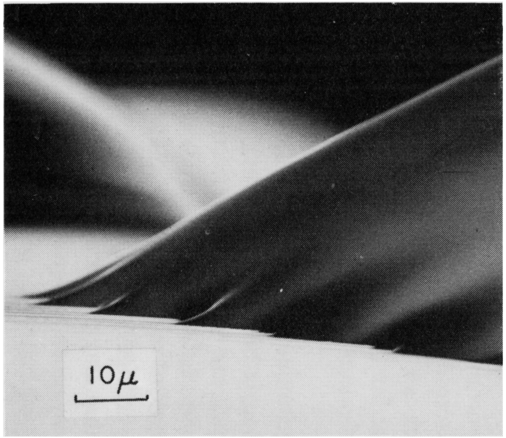

Fig. 2—As Fig. 1, but viewed across the grooves (Note the elongation of the drop along the grooves as a result of inhibition of spreading across the edges of the grooves, which thus act as capillary channels)

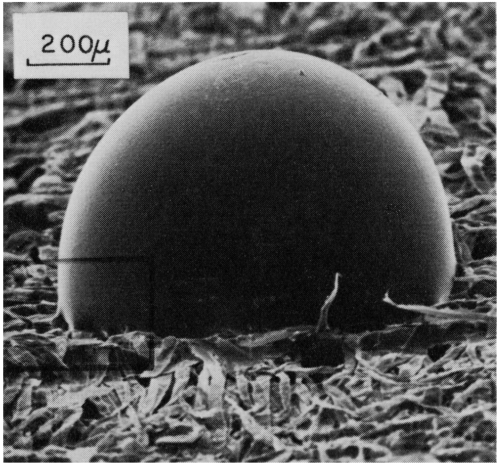

Fig. 3—Solid polymer drops on paper surfaces after spreading in the molten state PE on tissue paper

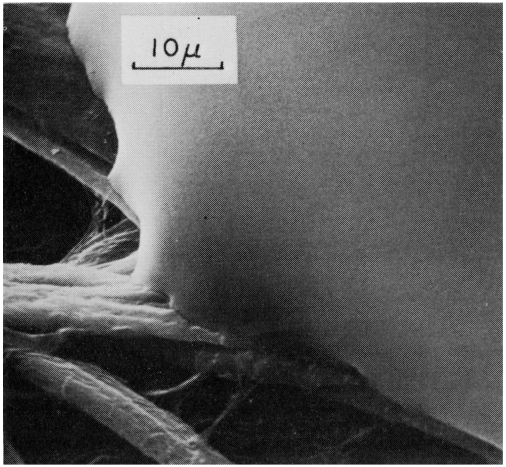

Fig. 4—As Fig. 3: edge of a PMMA drop on a rag content bond paper

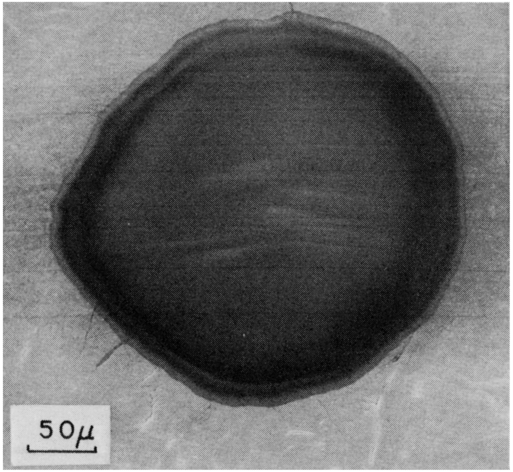

Fig. 5—PPE liquid drop deposited on super-transparent glassine showing top view

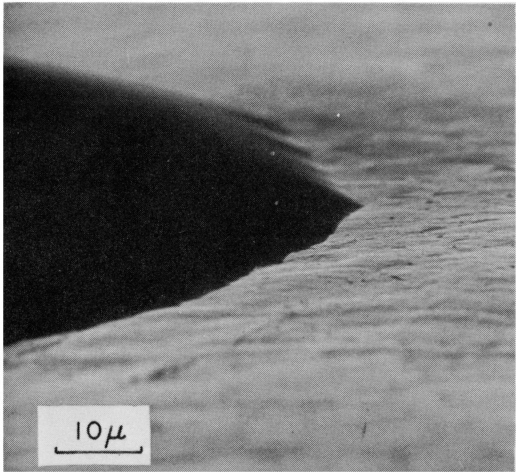

Fig. 6—As Fig. 5, showing side view with top views (*left*) and side views (*right*)

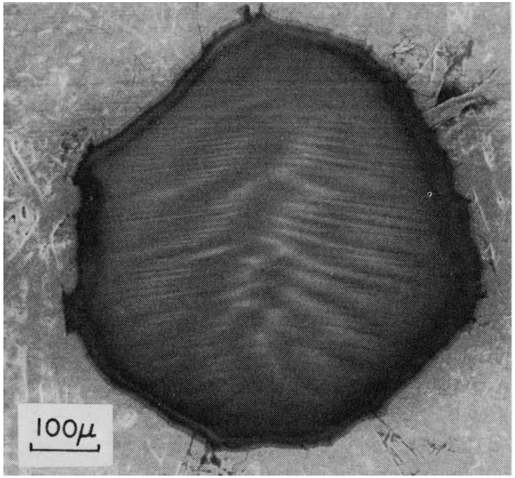

Fig. 7—PPE liquid drop deposited on opaque glassine showing top view

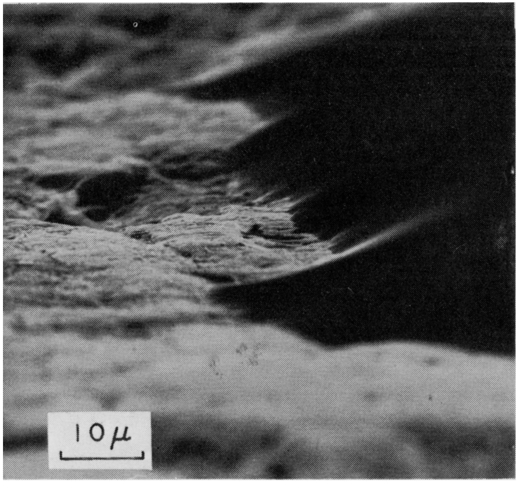

Fig. 8—As Fig. 7, showing side view

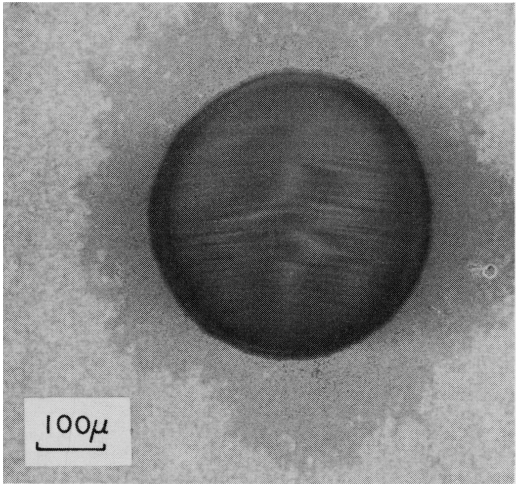

Fig. 9—A PPE liquid drop deposited on a smooth cast-coated paper: top view showing penetration into the porous substrate

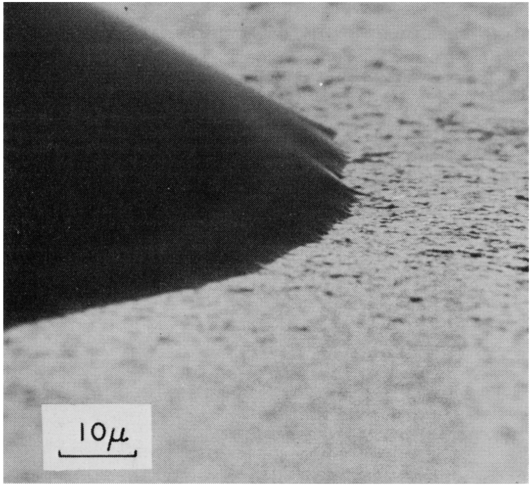

Fig. 10—As Fig. 9: side view showing irregularities in the contact line and θ

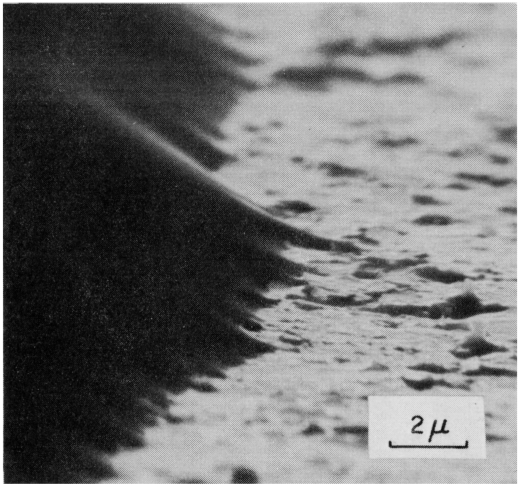

Fig. 11—As Fig. 9: another side view showing irregularities in the contact line and θ

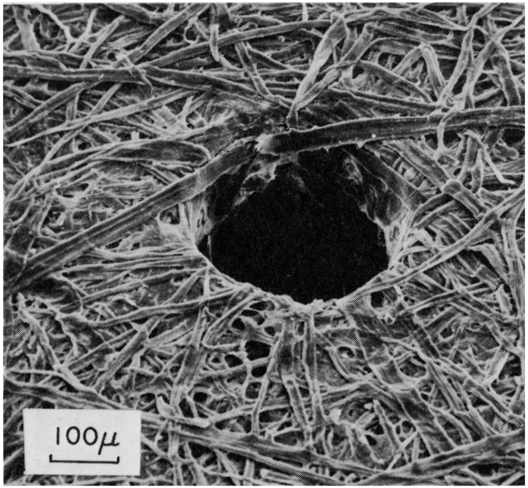

Fig. 12—View of a pinhole pierced into bond paper used for feeding liquid on to the surface in dynamic studies

that are apparent at higher magnification (Fig. 10) tend to pull out the liquid. Higher magnification (Fig. 11) reveals this behaviour more clearly; we suggest that these local protrusions from the drop result from particles of pigment in the coating material, which have a relatively higher surface free energy than the cellulose. Here, the macroscopic $\theta = 30°$, whereas θ measured locally (Fig. 11) varied considerably, approaching $\theta = 0°$ at the end of a protrusion.

Dynamic studies

To observe dynamic spreading, PPE drops were fed on to the gold-palladium alloy-coated paper surface through a small hole (Fig. 12), aligned with a hole drilled into a special sample stub attached to a small bore flexible tubing, through which liquid was driven from an external supply. By operating the SEM in the TV scan mode, the image of the spreading drop was recorded continuously (Sony AV3650 Videocorder) on $\frac{1}{2}$ in video tape, to provide resolution down to 1 μ. When the video tapes are viewed,* they reveal clearly how the advance of the contact line depends upon local fibre orientation. With both newsprint and a medium quality bond paper, the advance of the contact line is arrested when it meets a fibre lying across its path until the liquid acquires sufficient spreading pressure to overcome this local spreading resistance.(1) This was observed also with the stationary drop on opaque glassine (Fig. 7), in which individual fibres still existing appeared to resist spreading of the liquid at rightangles to their axes. The behaviour of fibres lying approximately parallel to the direction of spreading proved interesting, particularly with newsprint fibres, when some fibres enhanced the local spreading rate. On closer inspection, these fibres had parallel ridges that created capillary channels, analogous to those in Fig. 1, which increased the local spreading rate. Fibres in the bond paper, being smoother, yielded more regular spreading of the liquid. With both papers, penetration of liquid beneath the surface was evident.

Conclusion

THESE studies demonstrate that the macroscopically measured angle of contact of a liquid on a rough surface may represent a mean of a distribution of local contact angles resulting from the surface roughness and heterogeneity. As a result, measuring the contact angle on a rough surface by the conventional low-power goniometer method may be very misleading. Furthermore, paper surfaces often consist of fibres with sharp edges,(3, 4) which we have shown(1) in model experiments to have a significant inhibiting

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* At the symposium, 16 mm ciné-film transcriptions of video tapes (with some loss of resolution) of spreading drops were shown

effect on the spreading of a liquid. The surface morphology of fibres also has a pronounced influence on spreading and absorption behaviour of liquids and warrants further study. We believe that SEM studies of this kind can provide valuable insights into wetting, spreading and absorption phenomena in paper.

Acknowledgements

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Transcription of Discussion

Discussion

Chairman The coating of paper is an ancient art—the Chinese did it 2 000 years ago (surface pigmenting their paper), also the Turks in the 15th and 16th centuries (treble treatment). Machine coating was introduced in this country for the first time in the sixties of last century. Now the surface treatment of paper and board is a growth industry, with web widths on or off the machine up to 10 m for printing papers on an airknife coater and speeds up to 1 000 m/min on a blade coater. What is our scientific understanding of these paper treatments after doing them for the last 2 000 years?

Prof. B. G. Rånby I have one comment about the possibilities of making paper less permeable. As pointed out by Prof. Stannett, the only reasonable way is to put a coating on as a continuous surface layer. Any attempt to disperse particles or latex in the fibre suspension or impregnate the paper to decrease permeability are much less effective.

There is one more point I wish to make related to the problem of having polymers other than those now commercially used to decrease the permeability by surface coating. The new polymers that have been brought on to the market recently—plastics like Barex and Lopac containing acrylonitrile—are very impermeable, they have a high mechanical modulus and they can also be used within a wide temperature range, which makes them favourable as packaging materials. It has also been stated that these new materials have advantages from an environmental point of view: we have to be careful there. PVC develops hydrogen chloride when burned, which is not really poisonous, although it is an acid. We must look also at the burning of the acrylonitrile polymers: at low temperature with insufficient oxygen, they give hydrogen cyanide, which *is* poisonous. If you burn at high temperatures with an excess of oxygen present, these plastics develop nitrous oxides, which are rather detrimental to the environment. The same is true for other polymers containing nitrogen—polyamides, polyurethanes and native products like leather and wool. We have to define the burning conditions carefully for temperature and oxygen flow to prevent formation of poisonous and otherwise undesirable gases.

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Mr J. R. Parker I would like first of all to thank Dr Youngs for so kindly talking to papermakers about this rather complicated subject. I think his approach is of great value and this will become more apparent in the further papers to be presented.

Here, we have in fact a macroscopic measure of the behaviour of fluids in unsaturated porous materials. This has great advantages over the approach for which a model is needed. This is not to say that models are not of great interest and importance, but here is a means of describing the movement of liquids without making any assumptions about the nature of the material.

Dr Youngs' approach also gives the answer to a question posed by Dr Tollenaar many years ago, 'How can we explain the distribution of oil up a strip of paper during a capillary rise experiment?' He had to do this in terms of a rather complicated model based on interconnected capillaries. This experimental result, as we see now, can be subjected to quite a different sort of treatment and useful information can be obtained for application to other problems. This approach is relevant to the setting of inks on printing papers.

May I say a word of appreciation about Dr Oliver's contribution. His work reveals phenomena that are of great importance in the printability field.

Dr J. D. Peel Mr Gate, referring to your graphs from the mercury porosimeter apparatus, did your analysis of the results take account of the effect of the pressure of the mercury on the pore size distribution in the clay? The pressures were fairly high and would probably alter the pore size distribution as the experiment progressed.

Mr L. F. Gate This is quite a valid point. My answer to it is that we only get to about 20·7 MPa (3 000 lbf/in^2), which may sound a lot, but the local distribution of pressure inside a coating will in fact be much less than that.

We have also looked at the forces necessary to disrupt a coating by using the Talystep. By increasing the loading on the stylus, a point is reached when you begin to disrupt the coating and a track is left behind as the stylus passes over it. From this, you can, from the loading on the stylus, the area of contact and the time of contact, get an estimate of the forces necessary to start disrupting the coating—and these in fact work out to be something of the order of 69 MPa (10 000 lbf/in^2). By the fact that you can get pool values that agree with other methods, using materials you might expect to be crushed, you could come to the conclusion that it is not particularly important, as the local variation pressures within the coating under the intrusion pressures are not great.

Discussion

Dr E. L. Back With respect to both papers by Dr Youngs and Mr Gate, it might be appropriate to say a few words about the directional anisotropy of pores in paper. It means comparing the porosity and flow restriction in the Z-direction with that in the sheet direction. One way to quantify this comparison is by the effective pore radius for capillary flow by the Lucas-Washburn equation in these two directions. Fig. J shows the ratios of these two effective pore radii, that in the Z-direction divided by that in the machine-direction, for boards over a range of densities. These are rather thick boards made on Fourdrinier machines and the layered structure of paper increases this anisotropy. The ratio for the papers we tested is in the range of 0·01–0·04.

In these measurements, the same liquid is used in both directions, so the wettability does not enter this ratio. We found this to be true when we compared oil and water, so long as the papers were unsized or free from inherent resin.

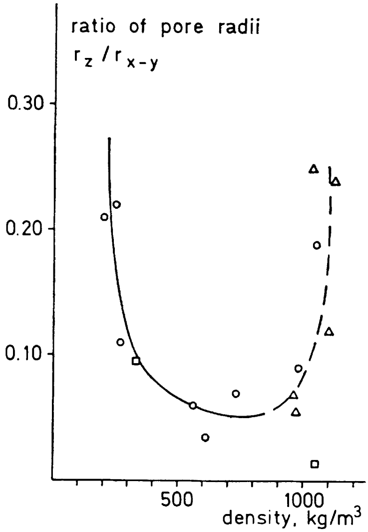

Fig. J

The ratios in this case were the same, within ± 10 per cent. For sized papers and papers with a large amount of mechanical pulp with inherent resin(such as newsprint), even if a surface agent was added, the ratios fell another one or two decades with water compared with oil. This might indicate that there is an additional anisotropy superimposed when resin or rosin is added to the paper. The distribution of this oleophobic compound will thus change the pore anisotropy.

Pore anistropy is important when evaluating the paper by impregnation, as well as for all printing.