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THE AREAL DISTRIBUTION OF LIQUID PENETRATION OF PAPER

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ABSTRACT

The penetration of fluids into paper is discussed with particular reference to the phenomenon of wetting. An experimental programme is described in which the distribution of penetration over the area of the sheet is measured.

The results indicate that considerable non-uniformity exists and, furthermore, an increase in the degree of sizing of the sheet leads to an increase in the non-uniformity of its wetting by aqueous fluids.

INTRODUCTION

The penetration of paper by liquids is a subject of the first importance to papermakers and paper users. In some instances we wish to maximise the penetration, or minimise the time for penetration to take place. In others, we wish to limit penetration and this is generally thought of in terms of maximising the time for penetration to be effected. The literature of the subject is extensive and it is not the purpose of this paper to attempt a complete review of it. In many cases the authors have been concerned with particular aspects of the application of liquids to paper for its treatment or end use, for example Hsu's work with printing inks (1), Windle and Beazley (2) on the fluid component of coating mixes or Hoyland (3) on penetration at the size press. For the earliest attempt at a formal, analytical approach to the subject we go back to Lucas (4) and the presentation of his work in English by Washburn (5) which gave rise to the well known Lucas-Washburn equation: $l^2 = \gamma \cos \theta rt/2 \eta$ in which l is the depth penetrated in time t by a fluid of surface tension γ , viscosity η and where the angle of contact between the fluid and paper is θ . Whilst it is now generally agreed, see for example (1) and (3), that this equation is not directly applicable in the interaction of aqueous fluids with paper, it does point our minds in the right direction in thinking about the subject. The dependence of penetration on the square root of time and the controlling fluid property being γ / η are useful and applicable concepts. The inclusion of the cos θ term implies the importance of wetting. Clearly, the paper surface must be 'wetted' by the fluid before penetration can take place. It has emerged from reported investigations that, for non-aqueous fluids, the Lucas-Washburn equation is applicable to paper. For example, Bristow (6) using a number of different oils obtained a linear relationship between liquid uptake and $\sqrt{t\,\gamma/\eta}$. It must, of course be emphasised that this was a bulk relationship, over a considerable area of paper which, possibly, accounts for why the underlying assumption of a straight, cylindrical pore structure does not invalidate its applicability.

When the penetration of aqueous fluids into paper is investigated the picture becomes more complicated. Van den Akker (7) calculated that, if water takes 100sec. to penetrate a typical sheet of paper, the contact angle, θ , of the Lucas equation would have to be 89.99984°. We may do the calculation the other way and show that if the contact angle were 0^0 the penetration time for a thickness of 100 μm, using the Lucas equation, would be 3×10^{-4} sec. This line of thought led to the view that paper sizing was brought about by modification of the contact angle of water on paper. The work of Bristow (6), already referred to, when extended to aqueous fluids showed another, interesting effect, namely, that when water is brought into contact with a paper surface, there is a measurable delay time before penetration starts. Wetting times of the order of 0.1sec. were observed and, also, he found that the addition of a surfactant to the water had no appreciable effect on the wetting time whilst it did substantially increase the rate of uptake, once penetration had started. This observation has recently been repeated, in both respects, by Lyne et al (8). Much of this work (Van den Akker, Bristow, Lyne) was done using dynamic testing devices which produced, on the uptake-time plot an intercept on the uptake axis, generally ascribed to a layer of liquid trapped by the rough surface of the paper. This effect is well known in size press investigations (e.g. Howarth (9)).

The effect of surface roughness in creating an immobilised layer on the surface, characteristic of all dynamic methods of liquid imbibition experiments, may be eliminated by the use of a static experimental technique. This is not to say, however, that the effects of roughness are completely eliminated by this procedure. It is, of course, well known that surface roughness has an effect on the wetting phenomenon itself (see, for example, the discussion of Haynes' paper in Fibre Water Interactions (10)). A static method was developed by Hoyland and his co-workers at UMIST in which, by the use of inserted electrodes, the passage of the liquid front through paper was directly timed. The method was further developed to include a measurement of the swelling of the paper by the imbibed water and these results have been reported (11). Among other things, they confirm the importance of the delay in starting penetration which, in the early stages of the work, we called apparent wetting time. Wetting time now appears to be the accepted term for this phenomenon.

EXPERIMENTAL PROCEDURE

The work now to be described came about as a result of difficulties encountered in some experiments with a size press. We wished to relate, if possible, the depth of penetration of fluid in paper applied by a size press to the hardness of the size press rolls. The rather obvious experiment was set up using size press rolls of different hardness, keeping everything else constant and measuring the depth of penetration of a starch solution by observing iodine stained sections (12). In analysing the results we found enormous variability in the observed penetration within samples, such that, to obtain significance in the results, we had to examine not less than 100 sections for each condition. In passing we may mention that the conclusion reached was that softer rolls gave a greater penetration than hard rolls, but the difference was small, 39% of thickness compared with 34%. There were, as may be expected, complications to the picture and a more detailed account of that work is called for. For the purpose of this paper, one conclusion reached was that the variability, from point to point in the sheet, of liquid penetration into paper needed some investigation. An indication that this variability may be due to uneven wetting of the surface is given in a much earlier paper by Knight (13). He used a moving applicator to put liquid onto paper, the applicator being followed by a suction device to remove all liquid not immediately taken up by the paper. The mottled pattern on the tested sheet clearly showed a variation in the wettability of the surface from point to point.

For our experiments, we used an adaptation of the apparatus developed by Hoyland and Field (3). Instead of the electrode timing system used in their work, a cine-camera was employed to obtain a pictorial record of the pattern on the top side of the paper. The method consists of bringing a liquid surface into contact with the under surface of a horizontal sheet of paper and monitoring the penetration of dyed water through it by taking a cine film of the upper surface. A general view of the apparatus is given in Fig.1.

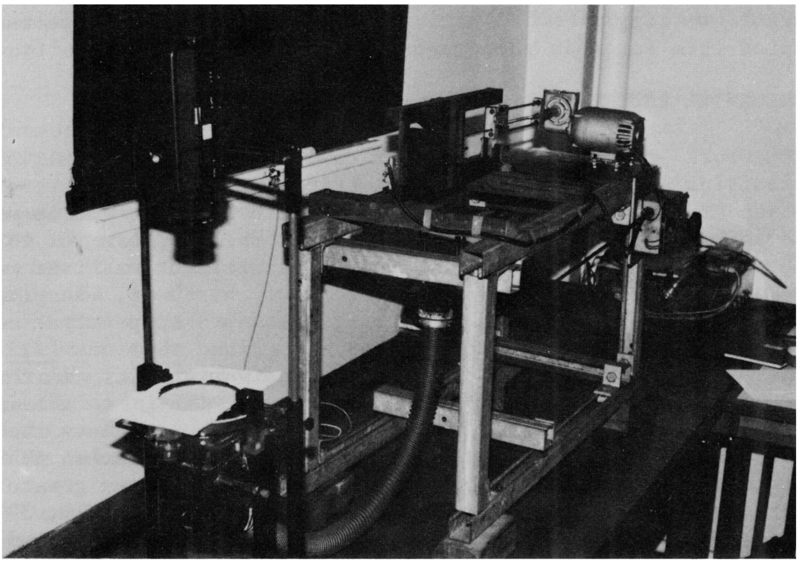

Fig 1—General view of UMIST wetting tester

The films were analysed with the Joyce-Loebl, Magiscan image analyser. This is essentially a black and white device, its operation depending on the appropriate setting of a grey level. A slight problem arose in that black and white Super 8 films are not available and so we used a red dye in the penetrant water and interposed a green filter before the camera. The camera used was a Eumig Nautica which operated at 18 frames per second. Its speed was checked by taking an action film of a digital watch. For filming, the top surface of the paper was illuminated by 4,150 watt tungsten lamps. A few preliminary runs established a working technique. After development, the films were run through the image analyser which, for each frame, gave a measure of the percentage of the area of the sample that liquid had penetrated. The picture element in the system corresponded to a square of 0.2mm side on the sample, the sample itself being a circle of diameter 11cm. At the

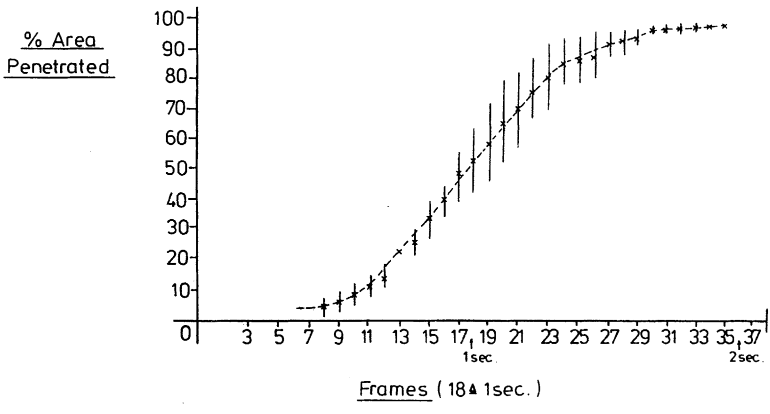

Fig 2—Area penetrated against time : waterleaf sheet

preliminary stage an experiment was done to decide whether the increase in penetrated area during a run was due to the generation of fresh, through paths or sideways spreading from established paths. Careful examination of successive photographs led to the view that the former method applied and sideways spreading was not an important feature of the results.

Figures 2 and 3 show results obtained with standard hand sheets made from a bleached sulphate pulp, Lumi Pine, beaten to 50 °SR.

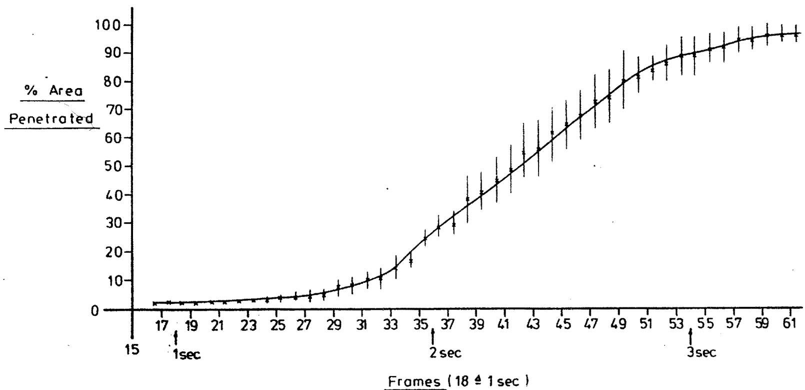

Fig 3—Area penetrated against time : sized sheet

The vertical lines indicate the spread of results obtained from ten runs, each with its own handsheet. It is clear from these results that three numbers will characterise the result obtained from each test. This is illustrated in Figure 4.

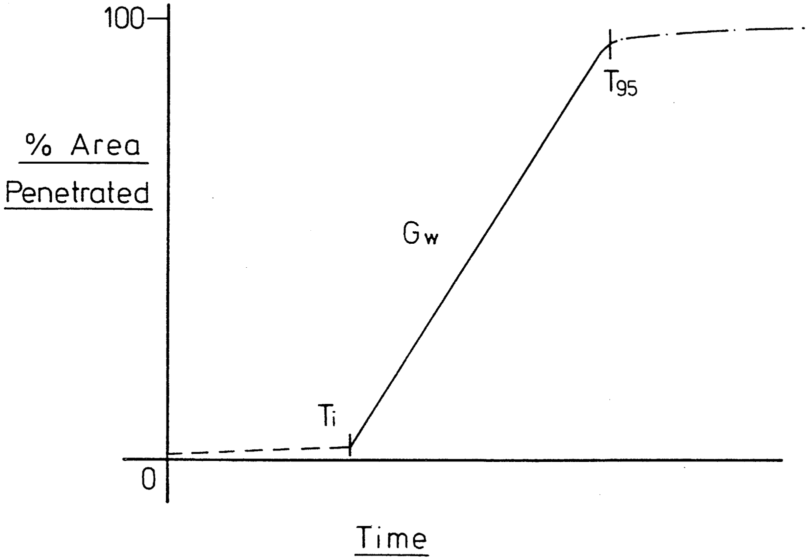

Fig 4—Components of area-time curve

The three characteristic numbers extracted from the penetration, time plots are:- Ti, the time of first penetration; Gw, the average gradient of the main body of the curve and T95, the time of complete coverage. For consistency of measurement, we defined Ti as the time at which 15% of the area had been penetrated and T95, as its name suggests, is for 95% penetration. The time, Ti, has two components, being the minimum wetting time of the under surface of the paper and the time of transudation through the sheet. We have assumed, that for any paper, the transudation time will be constant and the gradient, Gw, gives a measure of the uniformity of wetting time over the surface of the sheet. By using handsheets of different thicknesses, made from the same pulp, over a range of degrees of beating we checked the dependence of Ti on these factors. Figure 5 shows plots of Ti and thickness squared.

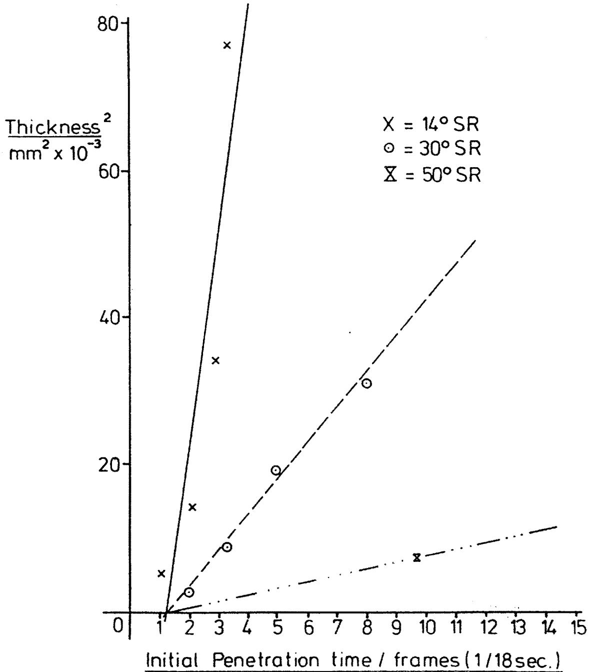

Fig 5—Ti as a function of sheet thickness

It is seen that, for the 14° SR and 30° SR beaten sheets, good linearity is obtained showing agreement with the Lucas concept. These two lines intersect on the time axis, giving a common wetting time of 0.067sec., which is within the range now generally accepted for waterleaf paper. The dependence of subsequent movement through the sheet, after the initial wetting delay, upon degree of beating is as would be expected. The line through the one point for 50° SR may, perhaps, be a little speculative.

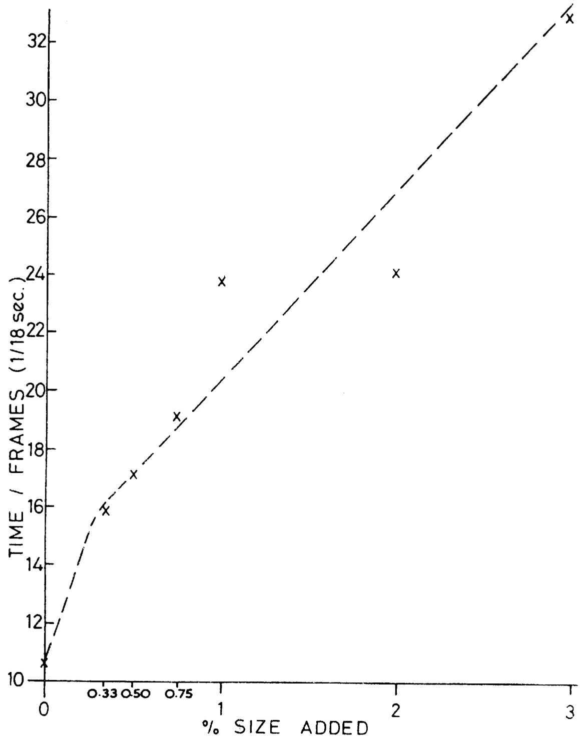

Fig 6—Ti against added size in the sheet

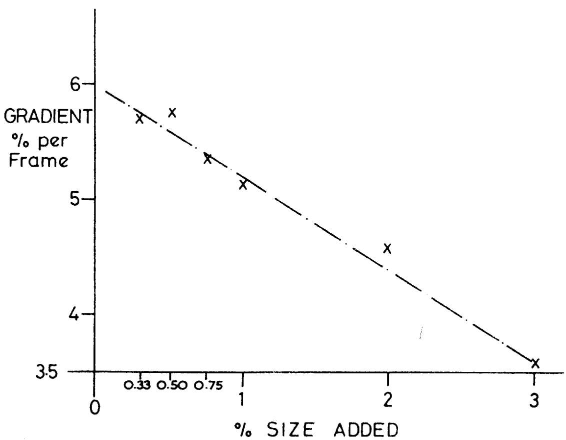

Fig 7—GW against added size in the sheet

For the interpretation of subsequent results, Ti is taken as the minimum wetting time, characteristic of the paper being examined, plus the small, transudation time. If we assume that this transudation time is constant over the sheet, then Gw is a measure of the uniformity of wetting time over the sheet surface. We know that wetting time is variable from Knight's results, already mentioned, and from an examination of some of our test sheets on the under side part way through test runs, obtained by stopping runs by lowering the liquid surface from the bottom side of the sheet. The constancy of transudation time has not been proved but is supported by the evidence of capillary-rise tests in which a substantially straight, horizontal wet line is obtained (14).

EFFECT OF SIZING ON AQUEOUS PENETRATION

Handsheets were made in the standard way with the addition of various amounts of a sizing agent. Results obtained from these sheets, after the sizing agent had been properly cured, are shown in Figures 6 and 7. These show, respectively, the effect of the sizing on Ti and Gw.

From Figure 6 it will be seen that the initial wetting time increases steadily with the degree of sizing, as would be expected. Figure 7 shows that increasing the amount of sizing has increased the variability of wetting time over the surface. This clearly opens the way for further work in sizing, to find a way of increasing the water repellancy of a paper surface without making it more variable in this respect.

COMMERCIAL PAPERS

Five printing papers, commercially produced, were examined. Because some of them had very long wetting times, the experimental arrangement was changed. The cine filming stage was eliminated by mounting the penetration rig directly under the Magiscan camera and using the built-in clock for timing. The very long wetting times obtained with some of the papers are a consequence of the experimental procedure having no driving pressure. The water surface is carefully brought into contact with the sheet in such a way as to avoid a driving pressure forcing it into the paper. Subsequent penetration is entirely dependent on wetting taking place followed by capillary imbibition. Results are given in Table 1, below.

Paper	Ti (sec)	Gw (%/sec)	60min. Cobb (gm^{-2})	Grammage (gm^{-2})
F	1.378	7.80	69	60
K	1164.5	0.0321	25	60
P	0.204	4.99	40	27
T	4842.2	0.0182	41	60
H	4968.7	0.0145	24	35

Table 1. Penetration results with commercial papers

Cobb test and grammage values have been included in the table. It will be seen that in broad generality, a high Ti goes with a low Gw. This is in agreement with our handsheet sizing experiment and indicates that a decrease in the uniformity of wettability over the surface generally goes with an increase in the degree of sizing of the paper. There is no close relationship between either Ti or Gw and the Cobb test value. We cannot say much about these papers. except that F and K are sold for use with one printing process and P,T and H for another. Also, paper F has been found to be significantly superior to paper K in ink-jet printing. Whether this superiority arises from its lower Ti or higher Gw is not known.

AN ALTERNATIVE FORM OF TEST

Clearly, in any practical situation the test described here, which may be called a static wetting test, is laborious, cumbersome and time consuming. The last stage of our work was to look for simplification. The Hercules sizing tester, which operates on a somewhat similar principle, was briefly examined. This instrument applies a small head of dyed water to the top surface of a test sample and monitors the reflectance of the bottom surface. It has an adjustable cut-off related to the percentage reflectance lost by the bottom surface becoming dyed, which relates to the percentage area penetrated. Using papers with varying degrees of sizing, the UMIST wetting test results for 95% penetration was compared with the Hercules tester results, the latter being set to record the time required for 80% reduction in reflectance. This is the recommended setting for the use of this instrument as a sizing tester. These results, plotted in Figure 8, show a linear relationship between the two tests. Figure 9 shows results obtained by varying the set point on the Hercules tester using two slightly different papers.

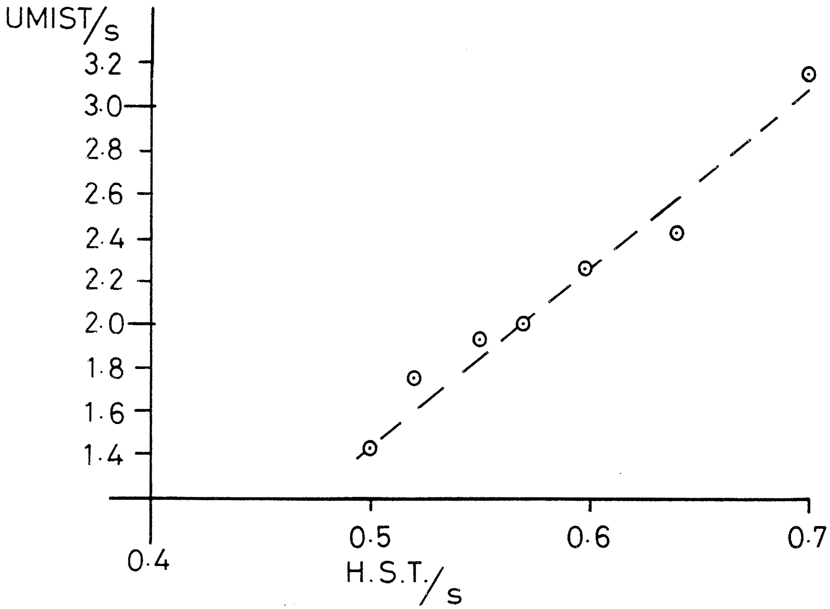

Fig 8—T95, UMIST against T80 Hercules

It would seem that a gradient figure, comparable to the UMIST Gw, could be obtained by using the interval between, say, 30% and 80% on the Hercules scale. There is scope for more work here.

CONCLUSION

The main conclusion that follows from this work is that, in the papers we have examined, the more highly sized the paper, the less uniform is the wettability of its surface. This could be a matter of some seriousness in that it is one source of mottled effects on paper where it is not wanted. For example, non-uniformity in the migration of binder from a coating mix into the sheet could cause variability in the ink-receptivity of the dried coating. It is suggested that, in considering methods of sizing paper, more consideration needs to be given to its uniformity, particularly with respect to the wettability of the surface of the paper.

ACKNOWLEDGEMENT

The authors express their gratitude to the Science and Engineering Research Council and the Hercules Powder Company for their support of M.K. Schindler, while doing this work, through a CASE award.

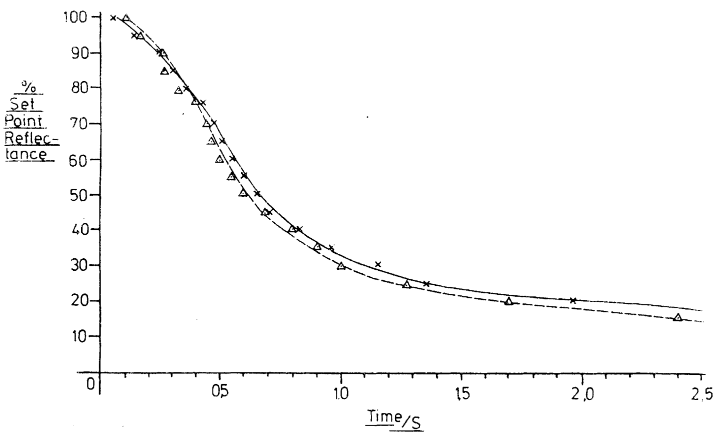

Fig 9—% Reflectance, Hercules tester, against time

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Transcription of Discussion

The Areal Distribution of Liquid Penetration of Paper
by P. Howarth and M.K. Schindler

Dr. J.S. Aspler PPRIC, Pointe Claire, Canada

Your reference 8 should read Lyne and Aspler, Tappi, Dec. 1982, page 98.

Although you stated that you were only dealing with water, would it be possible to use this apparatus with a low surface tension liquid like a mineral oil? This would allow you to look at non-uniformity in the physical structure. It would have interesting applications in newsprint, where the inks that are used set by penetration of mineral oil into the paper, and where the non-uniform penetration of the ink is as important as the overall penetration.

P. Howarth I have been very interested in your publications on this subject.

The original apparatus was used for a whole range of starch solutions and coating mixes. Some of the results are in Hoyland's paper in "Fibre Water Interactions".

We have not examined the drop in surface tension. I thought it was looked at by Bristow and by yourself that if you introduced a surfactant you did not affect the initial wetting time but you did affect the rate of transudation once the fluid had started going in. Is that not, now, a well authenticated result?

Aspler That is accepted. I am now interested in low surface tension oils, as well as aqueous systems with possibly variable surface tensions.

Howarth I think you will just have to try it and see.

Dr. R. Wasser American Cyanamid, Stanford, USA

I wondered if the major contribution to the gradient is not the formation of the paper in addition to other factors of which you talked. In other words, the most rapid penetration occurs in the thinnest spots of the paper and the slowest penetration occurs in the thickest parts of the paper. That would account for the change in gradient as you increase the sizing. Even if the sizing agent is uniformly distributed over the surface you would still expect to see that effect.

Howarth Yes, that is an interesting line of thought. We thought quite hard about how you could improve the hardness of the sizing without causing a deleterious effect on the uniformity of penetration. It may well be that the sizing does in some way reflect the formation of the sheet. Obviously, further very carefully planned work is required.

Prof E.L. Back STFI, Stockholm, Sweden

A 2 or 3 g/m^2 difference in Cobb values between top and wire-side is quite common. Have you observed the paper from top and wire-sides in your experiments? I believe this could give further insight into the nature of the areal distribution.

Howarth We standardised our experimental method by applying water on the top-side only. Your suggestion is very appropriate and one further step in our experimental programme should be to investigate the paper from both sides, as well as to include other variables but we have not got to this stage in the work yet.

Dr. R.H. Marchessault Xerox Research, Mississauga, Canada

The non-uniformity which would concern me would be on the micro scale and it would be measured by the circumference of the wetted area rather than by the total area. Have you given any consideration to this measurement?

Howarth No, we started with the size press experiment and were interested in the total non-uniformity over the area. Your suggestion could provide another route to investigating these properties but we have not pursued this as yet.

A. Wennnerblom SCA Nordliner AB, Pitea, Sweden

Did you find any improvement in the uniformity with increased storage time of the paper? It is certainly known that rosin size migrates and distributes over time.

Howarth That is a very interesting point. We have not investigated that as yet.

Dr. R.W. Davison Hercules, Wilmington, USA

Looking at your Figure 9 we can see that end points on the curve are achieved in 0.5 to 2.5 seconds. This is indicative of only mildly sized paper. I would consider 50 to 500 seconds to be more representative of sized papers. Am I right in assuming that you conducted your experiments on very mildly sized or waterleaf papers?

Howarth That is certainly true for the data presented in that figure.

Dr. J. Peel Beloit Corp, Bolton, England

The variability which appeared to be associated with sizing could be linked with the moisture pattern of the sheet, which in turn might be related to the formation. Your image analyser may be the perfect tool for analysing this possible effect.

Howarth Yes, that is a useful thought.

Ebeling I have a doctoral student working currently on this point to point correlation for the surface properties of multi-layer board and especially the effect of central ply formation on the variation of various properties. One of the main points which has emerged from this work is that if you are able to achieve very good formation in the central ply then the stiffness increases dramatically, which of course is very important from the point of view of savings in the cost of raw materials.