

SURFACE STRUCTURE OF COATINGS

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ABSTRACT

The positive intercept which appears on a graph of K and N ink absorption versus a function of absorption time has previously been interpreted as a measure of surface roughness. In the case of coated surfaces, evidence is offered that it is an indicator of a porous top layer of the coating with distinctly different properties from those of the main part of the coating.

It is shown that the total void volume of this top layer depends on both the capillary suction exerted by the substrate and on the speed of drying of the coating and its pore size is intermediate between that of the substrate and the main coating layer.

INTRODUCTION

In 1981 the author (1) presented a paper to the previous Fundamental Research Symposium which dealt with the analysis of coating structures by investigating the way in which liquid penetrated the coating and subsequently the underlying substrate. The liquid used was the well known K and N ink and the general results obtained are illustrated in Fig. 1. Ink was placed on the surface of the boards to be investigated and allowed to reside there for varying periods from 15 seconds to 36 minutes. A calibration procedure was developed which allowed the normal K and N reflectance values to be converted to true volume penetration values. A method was devised of calculating the pore sizes of the coatings by utilising certain items of information from curves such as

Fig. 1, namely the initial slope as the liquid passes through the coating, the second slope as the liquid penetrates the substrate and the total pore volume of the coating.

A feature of this kind of curve which was not made use of was the initial intercept. However it is clear that in any discussion of interaction between coated surfaces and printing inks the surface giving rise to this intercept is of vital importance. The volume indicated by the intercept is in many cases comparable to the total available ink vehicle and in such cases therefore it can be argued that the intercept is the most important part of the curve.

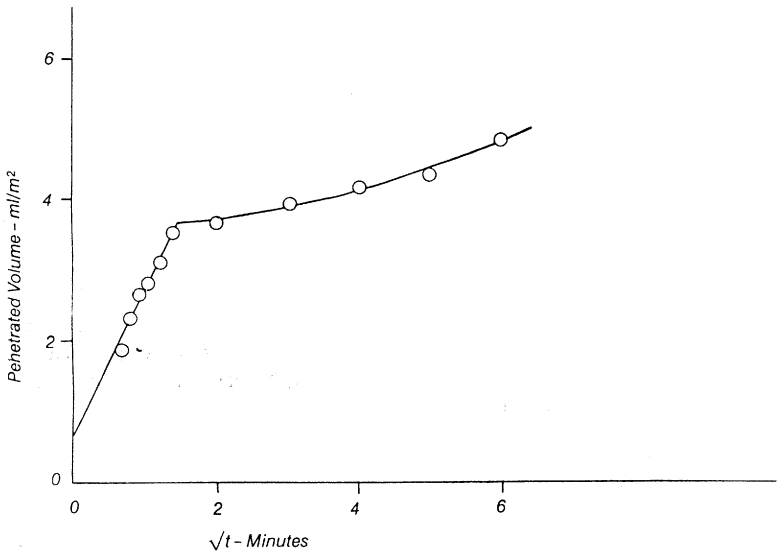


Fig 1—General form of Liquid Penetration curve obtained with K and N ink.

SIGNIFICANCE OF THE INTERCEPT

Chatwin, (2) who first devised the method of examining K and N ink penetration for varying periods of time, interpreted the intercept as a measure of surface roughness. His argument was that at the end of test, when the surplus ink is removed, some ink was left in the surface irregularities of the sheet and this amount was constant independent of the length of time that each penetration had been occurring. He therefore interpreted the first slope of the curve as one of true penetration into the coating structure and the intercept as indicative of the residual ink not removed at the end of the test and hence a measure of the roughness of the surface.

Our general experience of such testing over a period of some years led us to doubt this interpretation. A cast coated surface, for example, can frequently show a very significant intercept, whereas other much rougher coated surfaces can on occasions show very small intercepts.

This point was briefly touched upon during the discussion of the 1981 paper and the point made during that discussion is worth amplification.

The calibration procedure previously referred to consisted of allowing ink to penetrate into coated surfaces of precisely defined area for different lengths of time and for each time interval obtaining both the K and N reflectance value and the weight increase of the sample.

This data allowed a graph to be drawn such as shown in Fig. 2, and the important point of this graph and many others which have been produced in a similar fashion is that the lines always pass through or extremely close to the origin. Since K and N ink has a vehicle density of about 1 and a suspended pigment density of about 4, the ink material left in the surface roughness at the end of the test must be of the same nature as the material penetrating into the coating structure. The latter was shown to be vehicle only i.e. the pigment particles of the ink cannot gain access to the pore structure of the coating film.

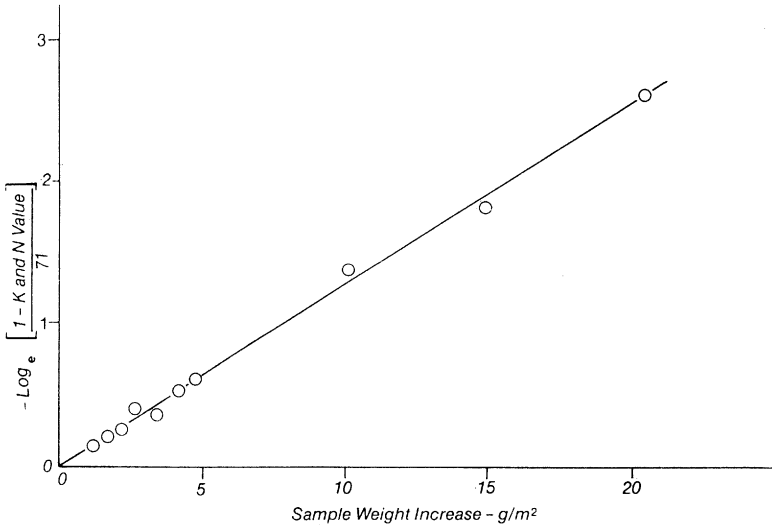


Fig 2—Typical calibration curve for determining penetration volumes.

The net conclusion therefore (assuming Chatwin's interpretation is correct) is that the surface roughness retaining residual ink must also be of such a size that pigment particles cannot enter it. This suggests that the roughness wavelength must be very much smaller than one micron. However since the intercept values show that the total volume contained must be of the order of one or more millimetres per square metre, this suggests a surface roughness profile of something in the region of two microns in amplitude and only a very small fraction of a micron in wavelength and clearly these two dimensions are irreconcilable.

An alternative explanation of the nature of such a layer is that it is a true porous structure of such a pore size that it is inaccessible to the pigment particles of K and N ink but at the same time much more absorbent than the main body of the coating structure since the ink vehicle penetrates it so rapidly than even by reducing absorption time down to four or five seconds it is rarely possible to detect any departure from the main slope of the first part of the curve.

It is obvious that for a better understanding of printing behaviour with respect to coated surfaces an attempt should be made to investigate the nature of this surface layer and its origin.

EXPERIMENTAL WORK

The essential objective of this stage of the work was to distinguish between the two pictures of the layer discussed above i.e. a true porous structure or a surface roughness. The difficulty of such work arises from the fact that liquid can penetrate and fill the layer whatever its nature in such a short time.

Eventually the approach that was decided on was to make use of Chatwin's original technique combined with our modified one. Chatwin performed his different K and N penetration tests on the same area of paper sample whereas in our experiments we normally choose a different area of the sample for each penetration time. It was argued that if the liquid volume corresponding to the intercept resided in a relatively open surface roughness layer at the end of the test, then after the removal of surplus ink had been accomplished there would be a further draining away of the surface liquid into the coating structure. If adequate time is allowed for such drainage to occur and is then followed by a second test for the same area, the total liquid penetrating during the two tests would be expected to be greater than the amount of liquid penetrating during one test of a duration equal to the sum of the two tests.

Several tests were carried out in this way on a series of different boards made by different manufacturers with times chosen so that in the shortest duration test, the advancing liquid front would be in the substrate i.e. it would have passed completely through the coating layer. Several different combinations of time were chosen e.g. two ten minute periods and one of twenty minutes, three ten minute periods and one of thirty, two fifteen minute periods and one of thirty etc. In all cases the time allowed between consecutive tests on the same spot for drainage to occur was thirty minutes. Finally the graph shown in Fig. 3 was produced by plotting the sum of volumes penetrating in the individual test periods against the corresponding penetrating volume for the total period in a single test.

It will be seen that there is no clear bias to one side or the other of the one to one line in this graph indicating that the volumes penetrating during the individual test periods remain in a fixed position within the pore structure during the waiting period between two consecutive tests i.e. no further drainage of residual surface liquid takes place. Since the advancing liquid front in all cases in this experiment was within the substrate, this implies that the liquid retained in the surface layer is subject to a capillary pressure numerically greater than that produced by the substrate. The effective pore size of the surface layer is therefore smaller than that of the substrate i.e. appreciably less than one micron. It is known from the relative speeds of liquid penetration that the surface layer must be of a larger effective pore size than the main coating layer and this experiment therefore shows that the surface layer pore size lies between these two extremes.

It was subsequently realised that it should be possible to confirm that the surface layer pore size is greater than that of the coating layer by repeating the experiment described above but this time ensuring that at the changeover period between two consecutive tests, the advancing liquid front was within the main coating layer rather than in the substrate. A further set of experiments was therefore carried out with the same samples in which the times used were 45 seconds for the initial penetration followed by a waiting period of 20 minutes followed by a further penetration time of 9 minutes 15 seconds on the same spot, and comparing the sum of these two penetrated volumes with that obtained from a single 10 minute test on the same sample.

To ensure that the void capacity of the main coating layer was sufficient to accept all the liquid drained from the surface layer, another set of experiments was carried out in which the times chosen were 10 seconds and 9 minutes and 50 seconds.

Fig. 4 shows the results of both sets of experiments and in this case it is clear that the points lie significantly to the left of the one to one line. The average offset is about 0.3 mls/m^2 indicating that this amount of additional drainage from the surface layer occurs during the waiting period under the conditions of these tests.

The average intercept volume for the boards examined was 0.9 mls/m^2 so that the drainage process removes about a third of the liquid content of the surface layer.

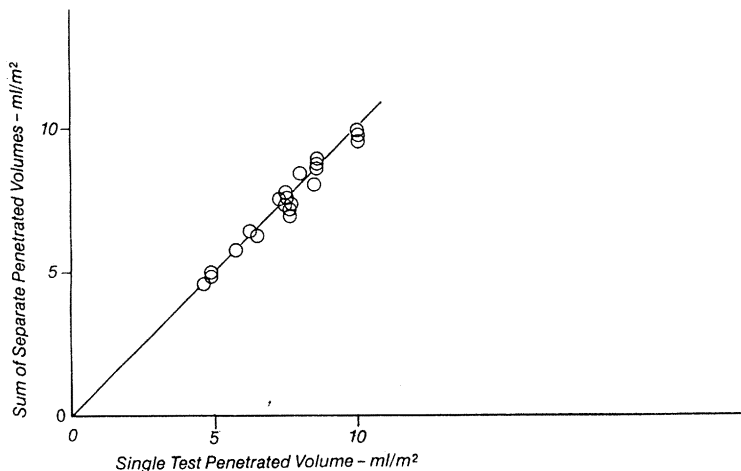


Fig 3—Comparison of single and multiple penetration values (liquid within substrate during waiting period).

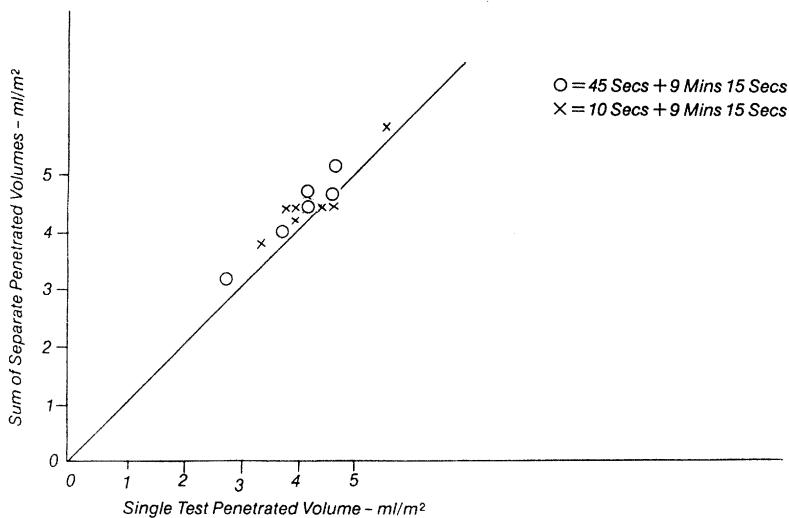


Fig 4—Comparison of single and double penetration values (liquid within coating during waiting period)

FORMATION OF THE SURFACE LAYER

If, as seems likely, coating films generally consist of two distinct layers of very different pore sizes, the question arises as to what part of the coating process causes this effect?

One obvious possibility is that of binder migration during drying of the coating. The argument here would be that movement of water from the coating into the substrate during the initial stages of drying would tend to carry binder particles with it and leave behind at the surface a layer which is relatively deficient in binder content. Two pieces of evidence from the 1981 paper argue against this.

Firstly if the data for capillary suction pressure caused by the substrate is plotted against the intercept of the K and N graph, for the eleven samples used in this investigation, it is clearly seen as shown in Fig. 5 that the greater the suction pressure the smaller the intercept. This does of course assume that there is a reasonable relationship between substrate capillary suction pressure when the penetrating fluid is an oil and when it is water.

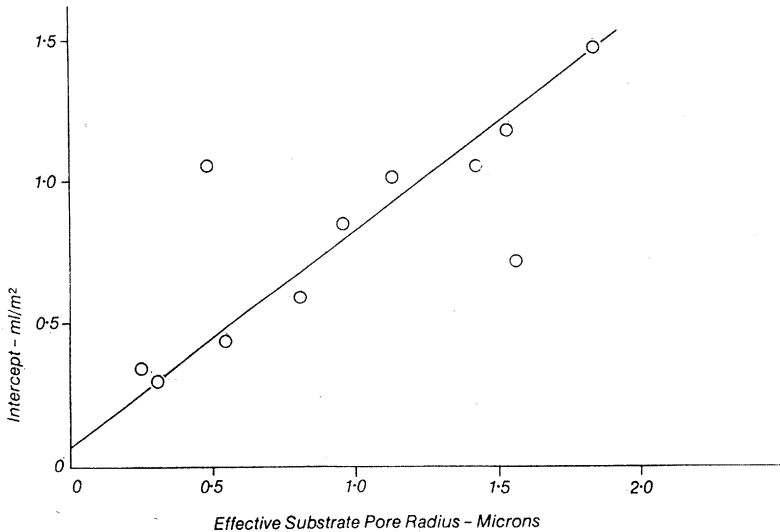


Fig 5—Effect of substrate capillary suction on intercept of Liquid Penetration Graph.

An even stronger argument perhaps is given by the two graphs shown in the 1981 paper for fluid penetration into coatings laid down on aluminium foil and on cellulose acetate. In these cases, of course, there would have been no water penetration into the substrate during the initial stages of coating drying and hence no obvious reason to assume the occurrence of binder migration. Despite this the intercepts shown by these graphs tend to be rather larger than those shown by coatings laid down on to the normal board surfaces.

If the notion of binder migration cannot be used to explain the effect, what else remains?

One possibility is the compacting effect produced by the viscous drag of the water as it moves through the coating structure. The relationship of Fig. 5 certainly suggests that the substrate suction pressure can produce such an effect.

A second possible mechanism of compaction is simply that due to the capillary pressure defect within the coating layer itself. This effect would arise as soon as the free surface water has disappeared and curved menisci begin to form. Its existence does not depend on water movement and its magnitude will increase as the structure becomes more compact.

In both cases it is likely that the total effect is not only due to the pressures involved but also the time for which those pressures can act and it would therefore be expected that there would be an influence of the speed of evaporation or intensity of heating applied in order to dry the coating. The sense in which this should operate is that the more intense the heating the more rapid the evaporation and the more pronounced the porous layer.

Very gentle heating or drying at room temperature on the other hand should allow the maximum time for the existing pore volume to consolidate the coating and to yield the minimum pore volume of surface layer.

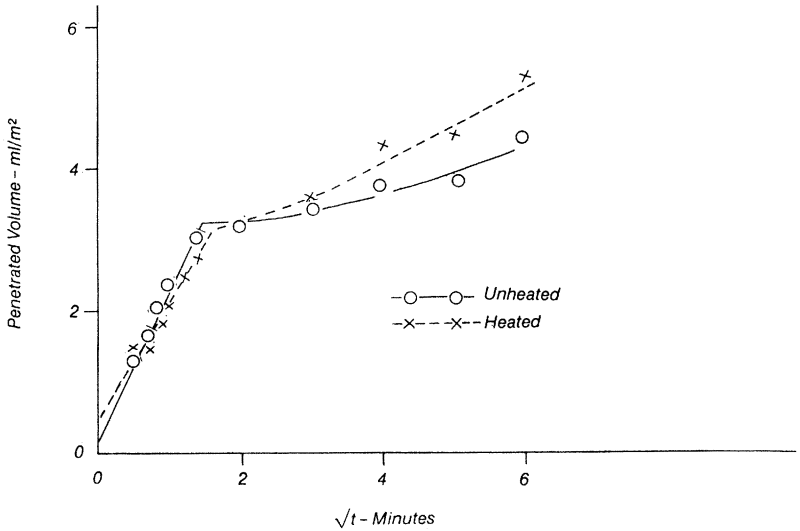


Fig 6—Liquid absorption for coatings dried with and without heat.

Fig. 6 shows two graphs obtained by coating in identical manners on the same substrate material, the only difference being that in one case the coating was allowed to dry at room temperature and in the other case fairly intense heating was applied so as to dry the coating within a few seconds. It will be seen that where heat was applied to dry the coating the intercept was approximately twice as great as in the case when no heat was used. It will also be noticed that the use of heat to dry the coating resulted in a steeper second portion of the curve indicating that the resistance of the coating layer to permeation is lower; in other words the rapid drying resulted in a more open main layer of the coating as well as a greater volume of the surface layer.

It is instructive to apply the technique of pore size calculation described in reference (1) to these two curves. The results of course, apply to the main coating layer only and not to the surface layer. The results of the calculation are given in the following table:-

Sample	Pore Radii (μm)		No. of Pores/ m^2	Pore Length (μm)
	Small	Large		
Hot Dried	0.0094	0.057	3.2×10^{13}	19.4
Air Dried	0.0093	0.021	6.5×10^{13}	55.6

This suggests that in the air dried sample the large pores are considerably smaller and since the two coatings are of approximately equal thickness the greater pore length in this case indicates that the fluid flow paths are more tortuous.

This observation of the effect of heat on pore structure of the main coating layer prompted a further look at the data of reference (1) and Fig. 7 shows a very clear connection between the capillary suction generated by the substrate and the calculated pore sizes of the main coating layer. As before a firm conclusion cannot be drawn from this fact because the capillary suction pressure in this figure has been calculated for oil absorption whereas the present argument is related to the suction pressure during water absorption.

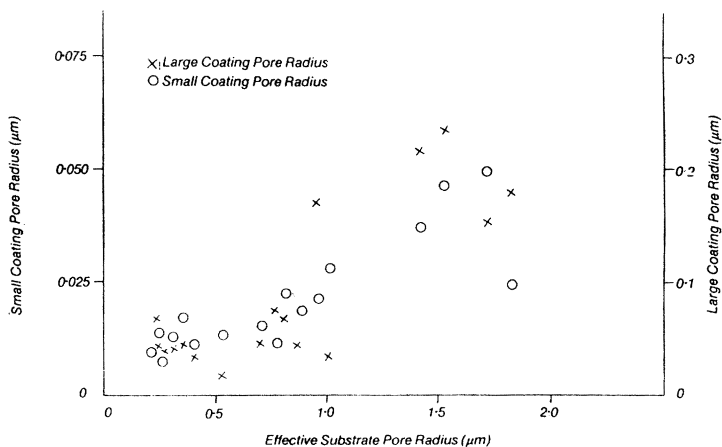


Fig 7—Effect of substrate capillary suction on Coating Pore Size.

It does seem that compaction effects occur both as a result of substrate capillary suction pressure and from slowness of drying and that these effects result in smaller pore sizes of the main coating layer and a diminished total pore volume of the surface layer. What is much less certain is the effect of compaction pressures on the pore sizes of the surface layer. Some information on this, however, can be inferred from indirect measurements such as those of varnish hold-out. It has been found that there is a general tendency for this to improve when for one reason or another the total pore volume in the top surface layer is diminished. Since in many of the cases examined the total volume of varnish being applied is insufficient to fill the void volume of the surface layer, it must be concluded that this is a result of reduced pore size.

CONCLUSIONS

The work described in this paper points to the conclusion that coatings on paper and board surfaces consist of two separate layers with distinct properties.

The surface layer is of a coarser pore size than the main layer. The total pore volume of this layer can be deduced from the intercept shown by the extended K and N graph but information on its pore size distribution is more difficult to obtain. It would appear to be inaccessible to pigment particles of appreciably less than a micron in diameter which certainly suggests that the pore sizes concerned are smaller than those of most paper and board substrates. This is confirmed by liquid penetration experiments in which it has been shown that the capillary suction effect which can be exerted by the substrate is not sufficient to cause any liquid drainage from the surface layer.

It can be inferred from observations of the K and N intercept combined with measurements of other properties such as varnish hold-out, that factors which cause a reduction in the total pore volume usually produce a smaller pore sized layer.

It has also been shown that a reduction in total pore volume and pore size of this surface layer is brought about both by increased capillary suction from the substrate during the initial drying stages of the coatings and by decreasing the rate of drying.

REFERENCES

1. Ranger A. E., The Role of Fundamental Research in Papermaking (J. Brander - Ed), Mechanical Engineering Publications Ltd., 685-705, (1983).
2. Chatwin C. E., Printing Technology, 16(2), 45-54, (1972).

Transcription of Discussion

Surface Structure of Coatings

by A.E. Ranger

D. Taylor Union Camp Corp, Princeton, USA

Was the board single coated or tandem coated and if tandem coated, were the two layers similarly formulated?

A.E. Ranger Most of the boards used were commercially produced and I would estimate that approximately half of them were double coated but I wouldn't like to be specific on the exact process or formulation.

Prof J. Silvy Ecole Francaise Papeteries, Cedex, France

Do you not think that the problem we have when we treat results from physical experiments on a sheet of paper or coating mathematically is related to the difficulty we have to extrapolating to the limits of the structure? So, if we take porosity for example, the porosity of the body of the coating is quite different from the porosity of the surface. At the surface of the sheet the diameter of a pore could be considered as being an infinite value. I think we have to take special care when extrapolating such curves as these to zero and bear in mind the physical meaning of the intercept at zero.

Ranger We are attempting to show that there is a difference between the material immediately below the surface and the main part of the coating. It is certainly true when you look in cross-section at a material with surface roughness that it is rather difficult to say that is where the surface ends and that is where the material begins. So what I am doing here in effect is to define the inside of the coating as that part which a fine pigment cannot reach, pigments of the order of 0.1 micron.

P.F Lee Mead Central Research, Chillicothe, USA

Did the K and N test show a mottled appearance or was it perfectly uniform?

Ranger In the general classification sense I would have said they were all fairly uniform.

Lee If there was some degree of non-uniformity, could I suggest an alternative explanation. I propose that instead of a variation in the coating in the Z direction an areal non-uniformity in the coating wherein at some points you could have relatively low coatweight and/or more penetration of the coating into the sheet. This could also explain a dualistic response of your coating to oil penetration.

Ranger I do not think we ever saw enough mottle to build an explanation on that basis.

B. Clarke UMIST, Manchester, England

Cast coated papers are so different to the others, would it be appropriate to ask how they behave in this sense?

Ranger Cast coated papers and boards were some of the first materials to make us suspicious of the "intercept equals surface roughness" explanation because the ones we looked at all showed a significant intercept, not much smaller than any other type of coated board. Incidentally, another trigger to our suspicion was the case of an ordinary laboratory coated board, air dried and uncalendered which was the only board we have ever seen which gave us a zero intercept. By any standards, it was a rough sheet and yet it gave us a zero intercept.

Ebeling Have you tried to correlate your extrapolated intercept values with quantitative data obtained from measurements of profile or really short time application of liquids? I am suggesting that you look at a 100 m secs or shorter contact times.

Ranger All our testing is done manually and you do reach a stage where it is practically impossible to shorten the contact time any further but up until that point we have not detected any evidence to suggest a deviation from the straight line.

Ebeling I would question the accuracy of the extrapolation of the intercept in your Figure 1. What worries me is that I do not believe this intercept method is sufficiently accurate to allow you to make judgements about what is happening on a nanometer scale.

Ranger I understand your concern but if you look at what we have published we are not primarily concerned with the numerical value of this intercept. What I would say is, that in virtually every sample we have ever looked at it is there and has never been on the horizontal axis and only once out of several hundred samples has it been anywhere near the origin. We are merely recognising that the intercept exists and then are trying to explain why it is there.

I.K. Kartovaara There are test instruments available in many laboratories which allow you to work with contact times as small as 10 m secs so I wonder why you need to extrapolate as you have done from manual measurements?

Ranger The explanation is that we do not have access to an instrument such as the one you describe and therefore we are restricted to carrying out manual measurements.

L. Smeets KNP Papier, Maastricht, Netherlands

Could it be a kind of pressure penetration so that when you wipe off the ink always you increase the capillary section so all the figures are shifted a little bit higher and you obtain an intercept?

Ranger No, I don't think that's the case.

Nissan May I add a few comments? To extrapolate back to the vertical axis is a mathematical device, but physically it is not permissible because that would mean an infinite acceleration of the liquid. Therefore, what one must assume is happening is a smooth approach to the origin, i.e. (0,0). Although the extrapolation to the origin is at a steep rate, it still provides a finite rate of acceleration of the liquid at the entrance to the capillary.

This raises two points. First, when experiments were done on pure liquids like water or alcohol etc., in glass capillaries of uniform diameter and the rate of change of height with time was plotted (both mathematically and from some observations) there was a very steep rise initially because when the capillary first touched the water, there was no resistance to the capillary force, except inertia. The rate of increase then decreased and finally, after a certain time, it followed the Lucas equation. Therefore, even with ordinary water in a uniform single-diameter tube you get, at very early times - of the order of milliseconds - some acceleration, followed by slowing down just as observed in these experiments reported here. Secondly, if the above capillary-entry phenomena do not provide a complete explanation for the steep rise of the curve from the origin to join the main part, then this could be explained by one of two further mechanisms. The first would be that large capillaries lead on to smaller ones. Alternatively, because we are dealing with a colloidal system - ink - it could be a time change in the slope because there is a separation of particles from the vehicle which will form new pores of smaller dimensions acting as a restriction. Which of these two mechanisms applies needs to be left to further experiments. There is a graph in Casey's book which shows an increase in Hercules sizing time for water as you treat the paper with more and more size. But for the same paper and size, the times for

ink increase much faster, and this is attributed to the colloidal nature of the ink and interactions with the pores themselves. So, I think we need to do more work in this area to explain the initial rates of imbibition of liquids by paper.

Aspler We use the high speed absorption apparatus developed by Dr. Bristow at STFI and we find that the relation between zero time extrapolation and surface roughness works very well for uncoated papers. We have done some work looking at low viscosity liquids on coated papers and I tend to agree with you that, here, we are not looking at a roughness effect but are seeing the effect of porosity.