Preferred citation: A.E. Ranger. Coating pore structure analysis by fluid penetration and permeation. In **The role of fundamental research in paper-making**, *Trans. of the VIIth Fund. Res. Symp. Cambridge, 1981*, (Fundamental Research Committee, ed.), pp 685–705, FRC, Manchester, 2018. DOI: 10.15376/frc.1981.2.685.

COATING PORE STRUCTURE ANALYSIS BY FLUID PENETRATION AND PERMEATION

A.E. Ranger
Thames Board Limited, Purfleet, England

Abstract

A fluid penetration technique is described which enables measurements to be made of penetration rate into coatings, of total pore volume, and of the subsequent permeation rate of fluid through the film. From these measurements, the number of pores and their length and diameter can be calculated assuming a simple model of pore structure. The lengths of pores calculated in this way are shown to be unrealistically large and a more complex model structure is postulated involving large and small pores serially connected. In order to determine pore sizes for this model it is necessary to generate an additional equation and this is achieved by measuring air permeation through the film. Pore sizes determined in this way are comparable in magnitude with those measured by other techniques.

Evidence is offered which suggests that air flow through coatings is molecular rather than viscous and that fluid pressures within the coating pore structure can be negative.

Introduction

Many of the important characteristics of pigmented coatings applied to paper and board surfaces involve interactions with liquids, e.g. printing ink vehicles and adhesives. These interactions are largely determined by the pore structure of the coating layer and methods of analysing this structure are clearly of importance.

The method which appears to have received the most attention is that of mercury intrusion. Because of its large contact angle, mercury will not penetrate a pore until a positive pressure is applied, and the required pressure increases with decreasing pore size. It is therefore possible to surround a sample with mercury, progressively increase the applied pressure and measure the penetrating volume at each stage. Although a complete picture of pore size distribution can be built up in this way, the method is open to criticism. It is clearly unable to distinguish between penetration into a uniform small pore and a small pore followed immediately by a large one, and for this reason tends to give results biased towards the lower end of a pore size distribution. This characteristic has been demonstrated by Climpson and Taylor(1) who compared their results with those obtained from direct microscopic analysis of the same sample.

Additional information on the larger pores in a system can be obtained by repeating the experimental procedure with a steadily decreasing pressure, following the extrusion of the mercury as well as its intrusion, and then making use of the hysteresis loop formed between the two curves in the way described by Gate and Windle(2). However, insufficient information has been published on this technique's application to coating films to assess its possible merits.

The intrusion technique would also seem to suffer from a lack of sensitivity when applied to coating films on porous paper and board substrates. Certainly most of the published work has been carried out on isolated films or films laid down on to non-porous substrates.

A method which can be applied to coatings on porous substrates is the gas-drive technique. Here, the sample is saturated with a wetting fluid which is then progressively removed from the various size pores by a steadily increasing gas pressure. The method has been described by Corte(3) and applied to coatings by Garey et al.(4). The interpretation of the experimental results requires a more idealised model of the pore structure than is the case for mercury intrusion and has been criticised on this account. In addition, it would also appear from the results to be given in this paper, that the use of the Poiseuille equation to describe gas flow through a coating layer might not be valid.

Other techniques which have been used are low temperature gas adsorption(5), a combination of specific surface area (from scattering coefficient) and total pore volume(6), and oil absorption(2). The latter investigation utilised a measurement of coating porosity and an assumed value of pore tortuosity in order to arrive at a value of pore size. Unfortunately, porosity is not an easy quantity to determine for normal thickness coatings on the relatively rough surfaces of paper and board, particularly when the investigator does not have access to the uncoated material.

Experimental Programme

The starting point for the present work was the technique described by Chatwin(7) which was designed to increase the information produced by the standard K & N ink penetration test. Instead of allowing the ink to penetrate for a fixed period of two minutes, Chatwin developed a procedure for removing the ink after a penetration period of only four seconds. After measuring the optical intensity of stain produced in the normal way he then applied ink to the same area for a further four seconds, and so on. In this way he built up a graphical representation of increasing ink penetration with time.

In our application, the ink for the different penetration periods was placed on different areas of the surface under examination as suggested by Parker(8), and the periods chosen ranged from fifteen seconds to thirty-six minutes. The resulting K & N values (drop in reflectance of stained area compared with baseboard reflectance arbitrarily set to one hundred) were plotted against the square root of penetration time.

The resulting curves, of which figure 1 is an example, clearly showed a discontinuity after a penetration time of around two to four minutes.

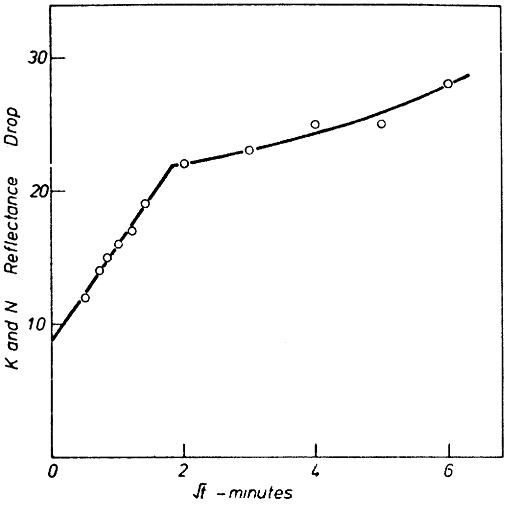

Fig 1—Example of extended K and N curve.

Several authors have suggested that the standard two minutes test period is sufficient for the ink to saturate completely most coating films. This suggests that the discontinuity marks the passage of the ink from the coating into the substrate.

To verify this, a complete K & N curve was produced for a hand prepared coating film which had been applied to Aluminium foil. Figure 2 shows that a point is reached where penetration ceases. However, it does not follow that this coincides with complete penetration of the coating film. It is conceivable that air, trapped between the metal and the advancing fluid. could exert a back pressure sufficient to inhibit further penetration.

To obtain further information, a similar film was laid down on to a sheet of transparent plastic. In this case, since penetration of the ink produces a high level of transparency of the coating film, it is necessary to back the sample with a constant white surface when measuring K & N values.

The reflectance measurements were made, at each penetration time, from both sides of the sample. If the ink has only partly penetrated the film, it is clear that the measured reflectance will differ depending on the viewing side. At complete penetration, however, the sample is optically symmetrical and the two measurements become equal.

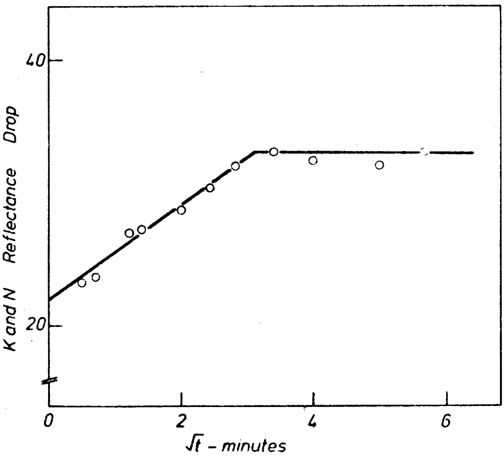

Fig 2—K and N curve for hand coating on aluminium foil.

Figure 3 shows that this merging of the two sets of readings coincides with the cessation of penetration, i.e. penetration does not stop (or even fall below the theoretical rate) until the plastic barrier is reached.

The similarity between the times taken in the previous experiments for complete coating saturation to occur and the times of the discontinuities in the K & N curves obtained with coated board samples, strongly supports the view that these discontinuities indicate the passage of fluid from coating to substrate.

Further support for this interpretation comes from two other considerations.

Firstly, a reduction in penetration rate at this point is what would be expected. The fluid is passing from a fine pore system to a relatively coarse structure. The capillary driving pressure (2γ/a for a circular capillary tube where γ is the fluid surface tension and a

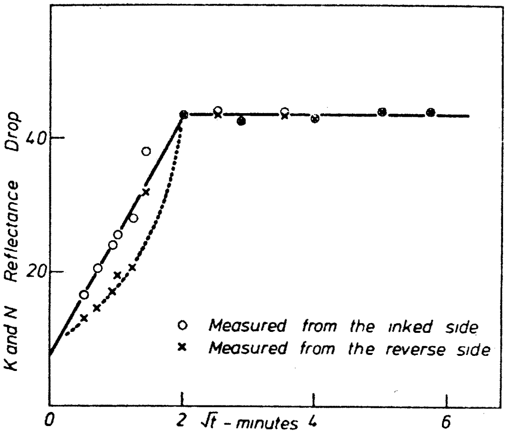

Fig 3—K and N curve for hand coated plastic film – reflectance measurements from both sides of sheet.

is the tube radius) will therefore fall significantly at the transition. The viscous drag, on the other hand, will remain sensibly constant since this arises from flow through the saturated coating behind the advancing menisci. A substantial drop in penetration rate is therefore inevitable. How sudden the drop is will depend on the uniformity of thickness and structure of the coating layer.

Secondly, again because the substrate is a much coarser structure, the resistance to flow offered by the substrate will be very small compared with that resulting from flow through the coating even at substantial penetration levels into the substrate. Penetration into the substrate would therefore be expected to follow an equation of the Poiseuille type (constant resistance to flow) with the volume flow being proportional to time rather than its square root. The points on the curves to the right of the discontinuities do in fact fit a linear relationship with time better than a square root one.

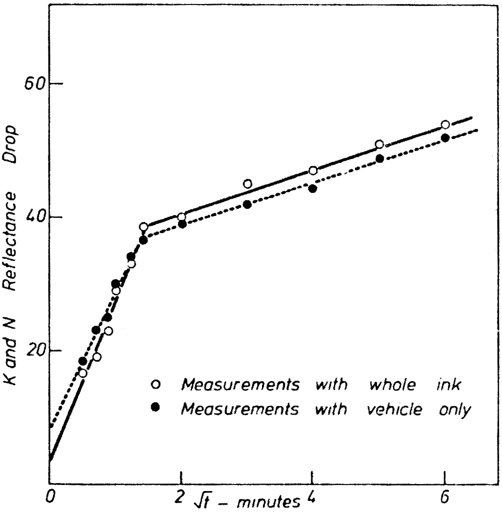

Fig 4—Extended K and N curves for whole ink and vehicle only.

Once this interpretation has been accepted the way becomes clear to convert the K & N system to a technique for quantitative pore structure analysis. However, there are still several preliminary steps to be taken.

Firstly, the nature of the fluid which penetrates the coating must be established. To do this, a small quantity of K & N test ink was centrifuged to obtain the vehicle free of pigment. A complete curve was obtained with this fluid as well as one with the whole ink on the same sample of board.

Figure 4 shows differences between the two curves which are small but may be significant. However, bearing in mind the fact that the viscosity of the whole ink in this case was some twenty times greater than that of the vehicle, the closeness of the two values of elapsed time to the discontinuity suggests that it is the vehicle alone which penetrates the coating when the whole ink is used.

The viscosity, surface tension, and density of the centrifuged vehicle were next measured by standard techniques.

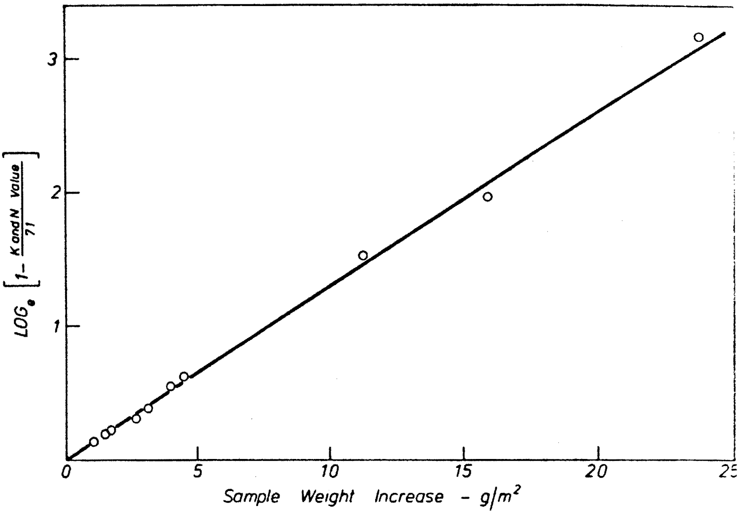

Fig 5—Relation between K and N value and weight increase.

Finally the ink being used was calibrated i.e. the relationship between the conventionally measured optical depth of stain and actual volume of penetrated vehicle was obtained. This was done by using adhesive tape to define a 50mm x 50mm open area on a set of board samples and spreading the ink over the whole of this area during the tests. In addition to the reflectance measurements, the weights of the samples before and after the tests were obtained and the weight increases converted to vehicle volume. Penetrated volume and K & N value were found to be related by a simple exponential function as shown in Figure 5, and this relationship was used in subsequent work to convert reflectance values to volumes.

Structural Analysis - Simple Model

The model first considered is one in which there are N straight, circular cross section pores per square metre, of length L metres and radius R metres. The penetration of a fluid of surface tension γ and viscosity η into such a structure is simply determined by the well known Lucas Washburn analysis and can be expressed (assuming a zero contact angle) as:-

$$V = \pi N\left(\frac{\gamma R^5 t}{2\eta}\right)^{1/2} \qquad (1)$$

where V is the volume (cubic metres per square metre of surface) which has penetrated after t seconds.

Since γ and η have already been determined and the initial slope for the K and N graph gives a value of $V/t^{1/2}$, use of this equation yields a value of $NR^{5/2}$.

Total pore volume is next determined by extrapolating the initial slope line back to the volume axis and calculating the pore volume as shown in Figure 6.

This procedure begs the question of the significance of the intercept. Chatwin interpreted it as a manifestation of surface roughness, some surface ink being retained on the sample after the final surplus removal stage. Although there are some respects in which this explanation lacks conviction, it has been found difficult to devise a more plausible one. If it is accepted, then of course the interpretation given here of both pore volume and initial slope are also justified.

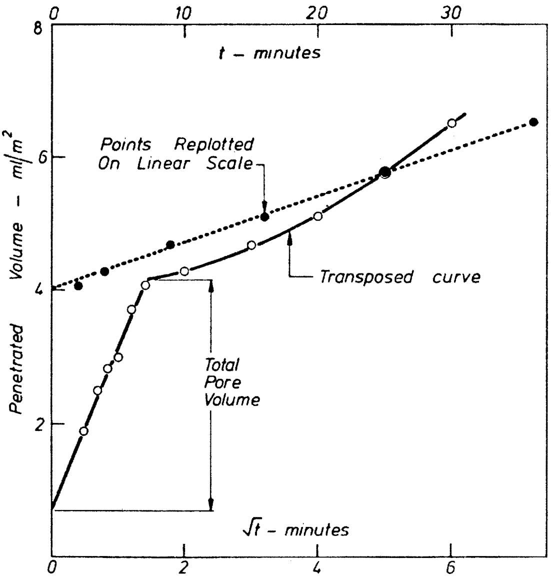

Fig 6—Determination of pore volume and form of 'substrate flow' curve.

In terms of the model, the total pore volume Q can be written as:-

$$Q = \pi N R^2 L \tag{2}$$

so that, equating this to the value obtained from the graph, a value of NR^2L is obtained.

Next, the penetration of the vehicle into the substrate is considered. As previously argued, this would be expected to follow Poiseuille's equation with the resistance to flow arising from the saturated coating layer and the driving pressure being determined by the pore size of the substrate. This can be written as:-

$$\frac{dV}{dt} = \frac{\pi N \gamma R^4}{4 \eta L r} \tag{3}$$

where r is the effective pore radius of the substrate. Referring again to Figure 6, the substrate penetration rate is calculated by replotting the points to the right of the discontinuity on a linear time scale and measuring the gradient of the best straight line through these points.

As a final step in the graphical analysis this straight line is then transposed to the square root time scale so that the exact discontinuity between the two parts of the graph can be determined.

The preceding three equations can be solved simultaneously for N, R and L provided an independent determination can be made of r, the effective pore radius of the substrate. This was achieved by a technique we refer to as `vacuum assisted ink penetration´.

Determination of effective pore radius

A small, perforated-top vacuum table was connected to a vacuum pump and gauge. The sample under investigation was taped to the top surface to seal the edges and leave a central exposed area that could easily be covered by K & N ink. The ink was applied and left for a sufficient length of time to ensure that it had completely penetrated the coating. A degree of vacuum was then applied to the back of the sample for a measured period, after which the surplus ink was removed and the intensity of stain measured in the normal way.

For this situation, in which the rate of penetration of fluid into the substrate is being increased by augmenting the capillary pressure, equation (3) can be generalised as:-

$$\frac{dV}{dt} = \frac{\pi N R^4}{8\eta L}\left(\frac{2\gamma}{r} + p\right) \qquad (4)$$

where p is the degree of vacuum applied.

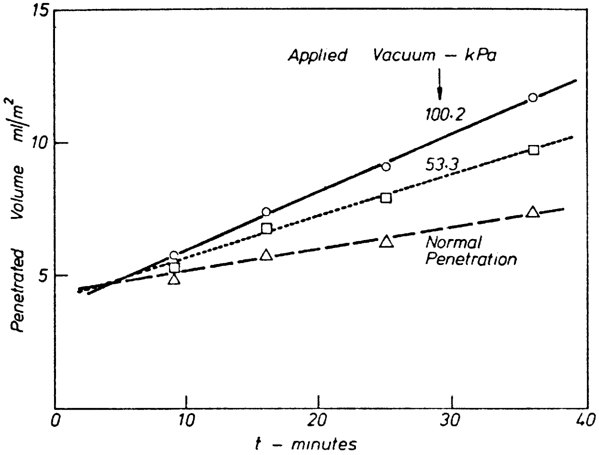

Fig 7—Increase in 'substrate flow rate' with applied partial vacuum.

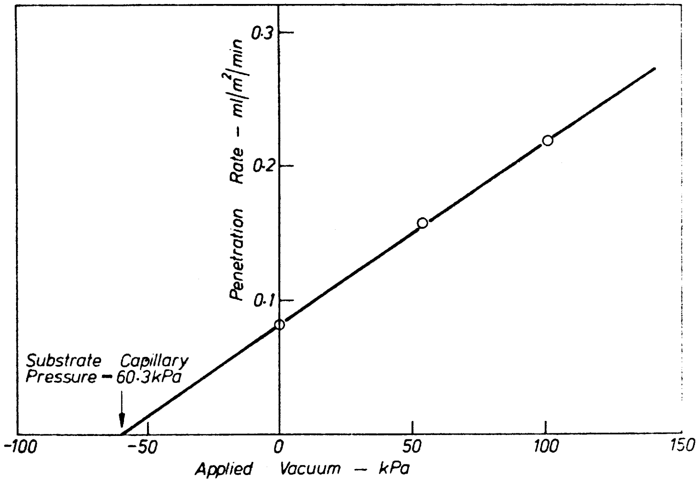

Fig 8—Determination of substrate capillary pressure.

Clearly, it is possible to measure the penetration rate for various values of p, plot one against the other and determine the capillary pressure as the intercept of the pressure axis.

Figure 7 shows a set of curves for one sample from which the values of dV/dt may be measured and Figure 8 shows the results of plotting these values against p.

Table 1 lists the capillary pressures and the effective pore radii calculated from these pressures for a selection of typical coated boards. The pressure ranges from 0.31 to 2.27 x 10^5 Pa. Since a value of 1 x 10^5 Pa is approximately equal to one atmosphere, any value greater than this signifies a negative pressure within the liquid, behind the advancing meniscus. This point will be more fully discussed at the end of the paper.

Sample	Capillary pressure (Pa x 10^{-5})	Effective Substrate pore radius (μm)	R (μm)	L (μm)	N (m^{-2}x10^{-12})
1	1.05	0.54	0.016	96	37.6
2	1.39	0.41	0.029	170	2.91
3	1.81	0.31	0.038	246	2.82
4	2.27	0.25	0.039	230	2.37
5	1.59	0.36	0.040	274	1.52
6	0.70	0.82	0.062	238	1.43
7	0.33	1.72	0.142	388	0.14
8	0.59	0.96	0.168	508	0.050
9	0.31	1.83	0.174	464	0.060
10	0.40	1.42	0.210	556	0.046
11	0.37	1.53	0.228	544	0.039

Table 1

Pore structure results - simple model

Pore Structure Results - Simple Model

Also listed in Table 1 are the values of N, R and L calculated by the simultaneous solution of equations 1, 2 and 3. The values of coating pore radius, R, range from 0.016 to 0.23 μm and as such, are broadly in agreement with previously published measurements. Likewise, the values of N which range widely around 10^{12} per square metre (one per square micrometre), seem plausible. However, the results for pore length are clearly wide off the mark. It is unlikely that the tortuosity in a coating film could exceed a value of about 8 (see Gate and Windle(2)) and even this would lead to coating thicknesses from 12 μm to 70 μm, which, in turn, are 2-5 times too large.

It is easy to see, from the basic equations, that it is the requirement of sufficient pore volume that produces this result. A pore model which contained `capacity' units which did not materially contribute to the viscous drag would obviously allow the fitting of the appropriate equations without the requirement of excessively large pore lengths. It was therefore decided to apply the data to a model consisting of pores of alternate small and large diameter segments as shown in Figure 9. Any additional complexity of the model structure, however, requires at least one further equation for a complete solution to be obtained. In the case of the present work, the possibility of a fourth equation arose from an earlier investigation of air flow through coatings.

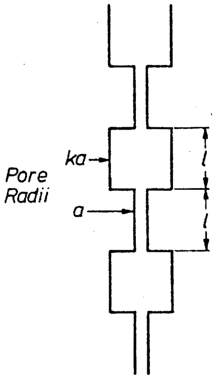

Fig 9—Sequential pore model.

Air Permeation Through Coatings

Corte(3) has described a technique for determining the mean pore radius of a paper by causing air to flow through the sample at various mean pressure levels. If the pressure is reduced sufficiently, the mean free path of air molecules becomes comparable to the dimensions of the pores and the gas flow changes from viscous flow to molecular flow. The pressure at which the air flow characteristics change can be detected and an appropriate value of pore radius deduced.

When an attempt was made by the author to apply this technique to coatings, no such change in flow characteristic could be detected. It was thought that this might be due to the coating pore sizes being comparable to the molecular mean free path, even at atmospheric pressure (mean free path of air at N.T.P. = 0.059 μm). This was verified by using Poiseuille's equation to predict air flows for the same samples as before having already determined N, R and L.

	Air flows for 1Pa pressure drop ($m^3/m^2/s$)							coating capill-ary
Sample	Predicted ($\times 10^9$)	Measured ($\times 10^8$)	Ratio	a (μm)	ka (μm)	2nl (μm)	N ($m^{-2} \times 10^{-12}$)	pressure (Pa $\times 10^{-5}$)
1	0.52	1.62	31.5	.014	.017	86	43.6	36
2	0.25	0.93	38.0	.012	.031	48	15.5	20
3	0.53	1.89	35.8	.012	.040	44	25.7	15
4	0.50	1.75	34.8	.013	.042	45	19.5	15
5	0.31	0.77	25.3	.017	.044	86	7.0	14
6	1.86	3.67	19.7	.023	.066	55	9.7	9.2
7	3.10	2.78	9.0	.049	.152	83	1.0	4.0
8	1.66	3.53	21.3	.021	.170	16	3.1	3.4
9	2.49	4.77	19.2	.024	.179	17	3.1	3.1
10	3.41	4.18	12.3	.037	.215	33	1.4	2.7
11	4.07	4.00	9.8	.046	.235	42	0.91	2.5

Table 2

Pore structure results - sequential model

Table 2 lists these predicted air flows, the air flows actually measured (by a modification of the Bendtsen method: see Figure 10) and the ratio of actual air flow to that expected.

The final figures show that air flow through coating layers is some 10-40 times greater than would be expected if the flow was governed by viscosity in the same way as is the case for liquid flow. It was therefore decided to use Knudsen's equation to describe air flow, which gives a fourth independent equation and therefore allows a model containing one additional geometric variable to be examined. The fact that the true flow is at least ten times more than would be predicted by Poiseuille's equation suggests that the use of a mixed regime equation such as that of Adzumi is hardly worth the penalty of the additional complexity.

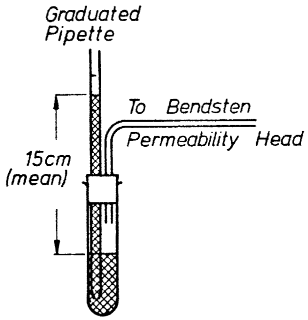

Fig 10—Apparatus for air permeability measurement.

Pore Structure Results
Sequential Model

The Appendix outlines the derivation of the four equations of this more complex model and the way in which they are solved simultaneously. As a check it will be seen that the first three of these equations reduce to those describing the simple model if k is put equal to unity.

Table 2 lists the major results from the solution of the equations for the same samples as before.

It will be seen that the larger of the two pore radii (ka) corresponds fairly closely to the single radius calculated from the simple model.

The number of pores per unit area with the new model is significantly greater but the total pore length (2nl) is now appreciably smaller than before.

If a tortuosity factor of 7 is applied to the average of these results, a coating thickness of 7.2 µm is obtained. This is considered to be a little on the low side and a tortuosity of 5 to 6 would seem to give a better fit. On the other hand, a wide range of tortuosity values, say from 3 to 9, would have to be used to account for individual results which in turn suggests that the assumption of a single value in coating structure analysis may give misleading results.

Investigators	Year	Method	Pore Diameters(µm)
Kraske	1960	Gas Adsorption	0.046-0.24
Trader	1971	Pore Volume and specific Surface	0.060-0.18
Garey et al.	1973	Gas Drive	0.10-0.50
		Mercury Intrusion	0.05-0.20
Gate and Windle	1973	Mercury Intrusion	0.12
		Oil Absorption	0.18
Garey et al.	1975	Mercury Intrusion	0.03-0.24
Climpson and Taylor	1976	Mercury Intrusion	Around 0.1
		Direct Observation	Around 0.25
Watanabe et al.	1980	Mercury Intrusion	0.03-0.12
Present Work	1981	Oil Absorption `a′ pore	0.02-0.10
		`ka′ pore	0.06-0.48

Table 3
Comparative Pore Size Values.

It is of interest to compare the pore sizes obtained with those reported previously in the literature and Table 3 shows that the two sets are broadly in agreement. Of particular significance are the results of Climpson and Taylor because of the two methods of measurement employed. It is possible that their direct measurements by microscopy be comparable with the `ka′ values, and their mercury porosimetry results with the `a′ values. this seems to be broadly the case.

Fluid Pressures within Coating Structures

It has already been pointed out that for several of the samples the capillary pressure within the substrate, as determined by the vacuum assisted ink penetration technique, was numerically greater than 10^5, which indicates the existence of a negative pressure.

Furthermore, it has been argued that the reduction in fluid penetration rate as the advancing liquid passes from coating to substrate is caused by a fall in the "driving pressure" (the numerical value of the capillary pressure) so that if the substrate fluid pressure is already negative, the pressure within the coating when the liquid is in this region must be even more so.

It is a straightforward matter to differentiate equation (6) and obtain an expression for the ratio of flow rates on the two sides of the discontinuity. This gives:-

$$\frac{\text{Flow rate in coating}}{\text{Flow rate in substrate}} = \frac{r\ (1 + k^2)}{a\ (1 + k^3)} = \frac{r}{ka}$$

i.e. the ratio is approximately that of the two capillary pressures with the average capillary pressure in the coating being determined by the 'ka' rather than the smaller 'a' pores.

Table 2 includes the capillary pressures calculated in this way for the samples being examined. All the values for the coatings are well in excess of 10^5 Pa and therefore indicate strong negative fluid pressures.

Although negative pressures in liquids can be induced in the laboratory and also exist in nature(9), the suggestion that they can exist in coating films is surprising. The state is one of metastability and, in the laboratory, requires considerable care in the exclusion of possible nucleation sites in order to produce it. This cannot conceivably be the case for a liquid penetrating into a coating.

On the other hand nature seems to be able to produce negative pressures without any special vessel or liquid preparation.

A possible clue to this puzzle may be provided by the fact that the present situation and the natural phenomena have one characteristic in common, namely that the liquids are confined within very small pores so that the radius of curvature of a vapour bubble could not increase beyond the pore radius. This is in constrast with laboratory systems in which the negative pressures are generated within much larger vessels or tubes. It may be, therefore, that a negative pressure, which exists by virtue of the smallness of the surrounding pore, is automatically stable because no nucleation site of sufficent size to produce instability can exist within that pore.

Conclusions

A technique has been developed for determining pore sizes in paper and board coatings using simple measurements and inexpensive equipment. The values obtained are in broad agreement with those determined by other techniques.

Application of the technique leads to the conclusion that coating structures consist of large and small pores sequentially connected.

A fluid penetration method which allows the determination of the pore size of the substrate without having to remove the coating film has also been developed.

Values obtained for the flow of air through coatings at atmospheric pressure suggest that the flow is molecular in nature and not viscous as normally assumed, but perhaps the most controversial conclusion is that fluid pressures during penetration into a coating film can be strongly negative.

REFERENCES

1. Climpson, N.A. and Taylor, J.H., Tappi, 1976, **59**(7), 89-92
2. Gate, L.F. and Windle, W., The Fundamental Properties of Paper Related to Its Uses (F. Bolam - Ed.), BPBIF, 1976, 438-451.
3. Corte, H., Fundamentals of Papermaking Fibres (F. Bolam Ed.), Technical Section, British Paper and Board Makers Association, London, 1958, 301-331
4. Garey, C.L., Leekley, R.M., Hultman, J.D. and Nagel, S.C., Tappi, 1973, **56**(11), 134-138
5. Kraske, D.J., Tappi, 1960, **43**(1), 73-82
6. Trader, C.D., Tappi, 1971, **54**(10), 1709-1713
7. Chatwin, C.E., Printing Technology, 1972, **16**(2), 45-51
8. Parker, J.R., ibid., 55-57
9. Hayward, A.T.J., American Scientist, 1971, **59**(4), 434-443

APPENDIX

Flow Equations for Sequential Pore Model (figure 9)

Dealing first with penetration, the instantaneous flow rate is:-

$$\frac{dv}{dt} = \frac{P_1 \pi a^4}{8\eta ml} = \frac{P_2 \pi k^4 a^4}{8\eta ml}$$

where m is the number of pore segments of each size which have been filled and P_1 and P_2 are the total pressure drops across the small and large sements respectively.

$$\therefore P_1 = k^4 P_2$$

and $P_1 + P_2 = P$, the total pressure drop

$$\therefore \frac{dv}{dt} = \frac{P\pi k^4 a^4}{8\eta ml\ (1 + k^4)} \qquad (5)$$

Now consider the filling of the next segment pair, assuming that m is sufficiently large to assume constant viscous drag. For the small segment:-

$$\frac{dv}{dt} = \frac{\pi k^4\ a^4}{8\eta ml\ (1 + k^4)} \cdot \frac{2\gamma}{a}$$

Since the segment volume is $\pi a^2 l$, the filling time t is :-

$$t = \frac{\pi a^2 l .\ 4\eta\ ml\ (1 + k^4)}{\pi\gamma k^4 a^3}$$

The filling time for the next (large) segment is found in the same way leading to a filling time for the pair of:-

$$T = \frac{4\eta ml^2\ (1 + k^3)\ (1 + k^4)}{\gamma k^4 a}$$

The incremental volume is $\pi a^2 l(1 + k^2)$ and assuming that this is small compared with the total penetrated volume:-

$$\frac{dv}{dt} = \frac{\pi a^2 l\ (1 + k^2) .\ \gamma k^4\ a}{4\eta\ ml^2 (1 + k^3)\ (1 + k^4)}$$

Substituting for m from:-

$$V = m\pi a^2\ l\ (1 + k^2)$$

separating the variables and integrating, one obtains:-

$$q_1 = \frac{v^2}{t} = \frac{N^2\pi^2\ a^5\gamma k^4\ (1 + k^2)^2}{2\eta(1 + k^3)(1 + k^4)} \qquad (6)$$

for unit area of the system (containing N complete pores) the total pore volume is:-

$$q_2 = V = N\pi a^2 n\, l\,(1 + k^2) \qquad (7)$$

where n is now the number of segment pairs in one complete pore.

The equation for substrate flow rate is obtained from (5) by putting m = n for the complete film thickness and using $2\gamma/r$ for the pressure:-

$$q_3 = \frac{dv}{dt} = \frac{N\pi\gamma k^4 a^4}{4\eta r n l\,(1 + k^4)} \qquad (8)$$

For molecular air flow, the treatment of Knudsen's equation is the same as for equation (5) and leads to:-

$$q_4 = \frac{dv}{dt} \cdot \frac{\bar{P}}{2PS}\sqrt{\frac{M}{2\pi RT}} = \frac{N k^3 a^3}{nl\,(1 + k^3)} \qquad (9)$$

where $\bar{P}$ is the mean pressure and P the pressure difference, S the sample area, M the gas molecular weight, R the gas constant and T the absolute temperature.

Finally, equations 6, 7, 8 and 9 can be solved simultaneously to give:-

$$\frac{q_1}{q_2 q_4} = \frac{\pi\gamma}{2n} \cdot \frac{k\,(1 + k^2)}{(1 + k^4)}$$ from which k is determined

$$\frac{q_1}{q_2 q_3} = \frac{2r}{a} \cdot \frac{(1 + k^2)}{(1 + k^3)}$$ from which a is determined

and $$\frac{q_2}{q_4} = \frac{\pi n^2 l^2}{a} \frac{(1 + k^2)(1 + k^3)}{k^3}$$ from which nl is determined

N is then calculated from Equation (7).

Transcription of Discussion

Discussion following paper 6.4, given by Mr. A.F. Ranger

Mr. J.A. Bristow, STFI, Sweden

I have one or two comments to make on Mr. Ranger´s interesting paper, although I am not sure I am able to answer the problem which he has just raised.

In a paper by myself and my colleauge Hans Bergenblad presented at the recent IARIGAI Conference in Key Biscayne, in which we discussed ink stain tests in general, we devoted quite a lot of time to the K and N test. Many of our results, though obtained from a different viewpoint, agree with those presented here.

However, I think Mr. Ranger should have mentioned the effect of paper roughness. Some of the results indicated in his curves may be fortuitous because he happens to have had very smooth paper. Chatwin´s description of the influence of roughness is probably correct, though his mathematics is unsatisfactory.

We confirmed that it is the vehicle in the K and N test which is absorbed though we proved this by a method different to that shown here, namely by calibrating the system with other oils of known viscosity. We also showed that some of the variation between different batches of K and N ink is due to differences in the viscosity of the oil phase. The manufacturers have been informed of this and are now trying to improve the uniformity of the product in this respect.

We too found these two-stage graphs, using the Cobb-Unger test, which gives gravimetric values directly for the absorption of oil at different times without the necessity for optical calibration. I would recommend this method over the K and N ink test for this kind of study.

We showed quite clearly that the first part of the curve is parabolic with time (linear with square root of time), while the second part is linear. Using oils of different viscosity, we obtain a pattern of different graphs, whose linear portions all extrapolate to the same y axis intercept. I believe that the value of this y intercept on a Cobb-Unger test graph roughly represents the total pore volume in the coating.

The major problem we encountered was that the transition from the parabolic to linear portions of the graph on the square root of time scale is not abrupt. There is severe levelling-off in the absorption rate. The transition zone between the coating and base must therefore be given considerable attention. Either there is an accumulation of binder at the interface, interfering with the migration, or perhaps there is some geometric difficulty in the oil´s transferring from one pore regime to another. I think it is impossible to relate any of the observations in the linear absorption regime to the pore structure in the coating until the behaviour in this transition zone has been clarified.

Mr. A.E. Ranger, Thames Board, UK

The last few minutes of my talk were concerned with this levelling-out of the square root plot (the transition from parabolic to linear time dependence). I think this is exactly what would be expected in the migration of the fluid from a narrow pore to a wide pore system, because the resistance to flow is provided by the upstream coating layer. All that changes is the capillary suction pressure, which is a function of pore size. Thus as soon as the liquid encounters a large pore system, the capillary suction pressure drops sharply, reducing the rate of penetration.

We have found a gradual transition, such as Mr. Bristow mentions, on some occasions, and have interpreted this as indicative of coating thickness variation across the sheet.

Prof. J. Silvy, Ecole Francaise de Papeterie

Why is the Carman correction to Poiseuille´s law not applicable here? In this correction the tortuosity appears as the square in the denominator, which brings the estimate of pore length, allowing for tortuosity, into agreement with the known coating thickness.

Mr. A.E. Ranger

I don´t think so. The maximum value of tortuosity we can reasonably expect in a coating is about 7. Applying such a tortuosity to the pore lengths produced by the simple model, the results are still much greater than the coating thickness.

Prof. J. Silvy

No. The tortuosity correction is 7^2, 49, thus bringing the coating thickness into a reasonable range. You are indirectly measuring the tortuosity.

Mr. A.E. Ranger

No, we can't measure tortuosity because we don't know the coating thickness with any precision. We know only within what approximate range it must lie. When the calculated pore length is 500 µm, we know that must be wrong, even with a tortuosity of 7. Introducing tortuosity into the equations as an additional unknown doesn't help since we don't know the coating thickness.

Dr. M. B. Lyne, Paprican

Following what Mr. Bristow said about roughness, I think you have very neatly trapped the roughness in figure 6. There, the extrapolation to zero time doesn't pass through the origin. Surely the value of the y intercept is the surface roughness of the material, giving the not unreasonable value of about 1 µm.

Mr. A.E. Ranger

I don't believe so, The extended K and N curve shows that there is a surface region of some sort. This could be true open roughness, or simply a region of greater porosity than the bulk of the coating layer. To differentiate between the two is a problem. The calibration curve of colour against weight starts precisely at the origin. We have obtained exactly the same values every time we've plotted the curve. This proves to me that whatever the surface region is, it is not accessible to the pigment, whose density is about 4 times that of the oil. Thus if the surface region is true roughness, it has to be of such a scale that the pigment cannot penetrate it. It could therefore be very small scale roughness but this would have only a small volume. I am therefore inclined to believe that it is a surface layer of high porosity which is giving rise to the intercept.

Dr. J.R. Parker, Bowater Technical Services, UK

I would like to congratulate Alan on his elegant and soundly based treatment of a very simple method. I would like to reassure him on this matter of negative pressures. It is fairly well established from the physics of fluids that such negative pressures can exist. Indeed, trees wouln't grow above 30.4 ft high without it. I would recommend that we try to contact someone from the Surface Chemistry Dept. at Bristol, for example Dr. Haynes, and ask him to make a written contribution to this discussion, for inclusion in the proceedings.

Mr. A.E. Ranger

Thank you for that comment. I have quoted a reference at the end of my paper on the general subject of negative pressures, which includes a discussion of sap rise in tall trees.

Dr. H. Corte, Wiggins Teape, UK

Knudsen molecular flow means that the molecules do not collide with each other when flowing, as they do in the case of normal diffusion, but bounce from wall to wall of the medium they are flowing through. This flow is therefore independent of the presence and number of other molecules, which is to say that it is independent of pressure. Therefore, a simple test of the presence of Knudsen molecular flow is that it should be indpendent of pressure for a given pressure difference, which is very straightforward to perform.

Mr. A.E. Ranger

The experiments I referred to in my presentation were of this kind.