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INVESTIGATION OF THE PORE STRUCTURE OF PAPER BY NOVEL POROSIMETRIC TECHNIQUES: APPLICATION TO SUPER AND SOFT-NIP FINISHING

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ABSTRACT

Over the years, large research efforts have been spent on determining the pore volume distributions of graphic papers. The pore volume distributions determine the absorption properties and light scattering properties of these papers and can be modified by a variety of calendering conditions.

In the present work we apply a variety of tests and void space modelling techniques to a series of five paper samples. The tests range from the standard to the novel, and all depend in some way on the void space structure of the samples. Three void space modelling techniques are presented. The first, traditional, method is based on the Laplace equation. The second model, developed by Yamasaki, implicitly assumes unconnected pores of a range of sizes, some of which saturate. The third, 'Pore-Cor', assumes a simplified three-dimensional structure. The samples all used the same 51gm^2 SC grade paper, the first being uncalendered, and the other four involving combinations of soft- and super-nip , with and without the prior application of steam.

Advanced imaging techniques such as optical microscopy and Environmental Scanning Electron Microscopy (ESEM) were used to obtain structural details of the paper cross-sections and paper surfaces, and with the ESEM it was also possible to investigate the effect of moisture on sheet structure.

Absorption properties of the sheets were determined by using the well-known Bristow equipment and newly-developed equipment for determining liquid absorption by fibrous sheets based on Liquid / Air Displacement Analysis (LADA). The LADA equipment applies liquid in a well-defined way which enables valid comparisons to be made with common absorption theories.

Results from the investigation with liquid porosimetry using water and hexadecane probe liquids show that there is considerable sheet expansion when the sheets are exposed to water. Undoubtedly this will lead to a change in the absorption process when the sheets are in contact with moisture. The shape of the absorption curves in both the LADA and the Bristow test equipment also indicate that this expansion will affect the absorption process. A simple mathematical model was also used to take this into account.

The mercury porosimetry data and the liquid porosimetry data were combined to yield a complete pore volume distribution curve for the sheet structure. These data were then used in the Yamasaki absorption model to simulate absorption, and were compared with the measured absorption values. These results show that the absorption can be simulated with a knowledge of the pore volume distribution curve and basic properties of the absorbed liquid. Large pores dominate the liquid absorption at short contact times (<1s), whereas the smaller pores dominate the absorption at larger contact times, as simulated with Yamasaki model. The overall time limit for absorption is naturally dependent on the total pore volume in the paper.

The combined porosimetry curves were also simulated using a recently developed three-dimensional void space modelling package, named Pore-Cor. This package generated three-dimensional structures with the same percolation characteristics and porosity as the experimental samples. The absolute gas permeabilities of these structures showed the same trend as the permeabilities measured by a Gurley Densometer. The simulated structures facilitate the mathematical investigation of other effects, such as the trapping of non-wetting fluids and the effect on permeability of the inclusion of colloids, Matthews (1).

INTRODUCTION

The demand for paper has increased ever since the change from written to printed books gave rise to the printing industry. With the invention of new printing technologies there is an even greater demand for papers that have specialised properties. Ink formulations, printing forms and printing pressures differ widely in the printing industry, and the pore structures and surface chemistry of papers need to account for these differences to generate a good printed image.

Paper consists predominantly of natural fibres from different types of pulps, with some inorganic filler pigments, and polymeric retention aids to increase the fines content in the structure, all bonded together to form a three-dimensional network. The properties of this fibre network are dependent upon the properties of the subunits, and the uniformity of their distribution in the three dimensions of the paper sheet. The fibrous material in paper is initially brought together by mechanical and surface tension forces, and then held together polar and non-polar forces between the molecules on the surfaces of adjacent fibres which give the sheet its mechanical strength. The strength properties of the sheet are dependent on the size of the contact area and the strength of the fibre-fibre bonding.

A model of paper structure may be considered in terms of fibre-based and molecularbased features. At the fibre level, paper may be viewed as a bonded network of elastic entities that form porous, permeable and inhomogeneous structures. The porous structure of paper is one of its fundamental qualities which affects most of the other properties of paper. In 1957, Corte (2) reported his thorough study of the structural aspects of phenomena in paper. The fluid flow through paper is controlled, apart from interaction and physical laws of transport, by the structure of the sheet. The statistical geometry of paper was outlined by Corte and Kallmes (3), and this work was later developed by Corte and Lloyd (4) in an attempt to extend the statistical geometry of multi-planar sheets to determine some of the structural and physical factors that control the fluid flow through such sheets.

The void structure of the sheet and the surface energies of the sheet components determine the optical and absorption properties of the sheet. Finishing a sheet by calendering will almost certainly alter the positions and orientations of the fibres and particles. These alterations may result in a change to the degree of bonding and the

distribution of void sizes, and hence may affect the strength and optical properties of the sheet.

The interaction between different liquids and paper has attracted a considerable amount of research over the years. These efforts have mostly been made in order to forecast the printing properties of various papers, and several theories and summaries have been published on the subject by Salminen (5), Kent and Lyne (6), Chatterjee (7), Bristow (8), Aspler (9), Ström (10) and Oliver and Mason (11). The present paper focuses on the combination of porosimetric techniques to characterise the pore structure of paper, new modelling techniques to simulate pore-level properties and the relationship between the pore structure of papers and the short time absorption of water into these papers. An important problem pursued in this study is that the void sizes and shapes in paper are changed when the porous substrate interacts with water. Salminen (5), Bristow (8) and Hoyland (12) all treated this problem by adjusting the path length the liquid had to travel to penetrate the expanded sheet. However only Schuchardt (13) seems to have considered the fact that a spontaneous change of sheet structure will result in a change to the absorption process. In other words, the wet pore structure will be different to the dry pore structure prior to wetting. However, Schuchardt (13) studied the effect of swelling superabsorbent fibres and its effect on the decrease of the pore size of the network. In the present investigation attention will be focused on how an increase in throat diameter might affect the absorption properties of the paper. This expansion of calendered sheets containing mechanical pulps has previously been studied by Skowronski (14).

Calendering technologies have been advancing rapidly over the last twenty years and it is well understood that calendered papers have better printing properties than uncalendered papers. Calendering improves the smoothness of the sheet at the expense of the caliper, thereby reducing the opacity of the sheet and increasing its density. One method of calendering to improve gloss and smoothness, without seriously reducing bulk is to use hot soft nip calendering. Another method to improve the response of paper to calendering is to increase the moisture content of the paper, which may be achieved by calendering on-line or by using a steam showers to spray the paper prior to the calender nip. Reviews of calendering technologies and processes have been given by Crotogino (15), Hilden and Sawley (16), Keller (17, 18), Kettle (19), Millington (20), Peel (21, 22), and Santkuyl (23). In this work we describe the use of a range of standard and novel experimental and modelling techniques to characterise the void structures of papers calendered under different conditions. The paper for this study came from a commercial SC grade paper that had been finished in a pilot-scale calendering study. This paper was calendered using two different types of calender, a supercalender and a soft nip calender. Five samples were selected; the uncalendered paper, a paper supercalendered at 800 m.min⁻¹, with and without steam pretreatment, and soft nip calendered papers calendered at 400 m.min⁻¹, again with and without steam pretreatment. These papers were tested for their standard paper properties including permeability, and advanced techniques were used to measure their pore size distribution, absorptivity and their expansivity.

THEORIES OF ABSORPTION OF LIQUIDS INTO PAPER

We now describe three theories of absorption of liquids into paper, ranging from an assumed fully accessible void geometry, through voids with saturation, to a three - dimensional void network with simplified geometry.

Laplace and Lucas - Washburn equations.

The current understanding in the literature of the interaction between liquids and paper, references 6 to 12, is still dominated by a form of the Laplace equation (24):

$$d = -\frac{4\gamma \cos\theta}{P} \tag{1}$$

where γ is the interfacial tension at the fluid surface, *P* the pressure, θ the contact angle and *d* the throat diameter. This equation is then combined with the Hagen-Poiseuille equation to yield the well-known Lucas-Washburn equation which describes the rate of liquid penetration into a porous substrate with time.

In this work, two types of fluid intrusion have been measured: mercury intruding into an evacuated sample, possibly containing residual air, and air intruding a sample containing hexadecane or water. During the intrusion of a non-wetting fluid such as mercury, P is the pressure applied to the non-wetting fluid which intrudes the previously evacuated sample, and d is the smallest pore-entry diameter intruded by the fluid at this pressure. For

wetting fluids, the equation only applies to the dynamic case, in which it is assumed that there is a quasi-static equilibrium between the driving capillary forces pulling the liquid into the porous network and the opposing forces created by the pressure drop P caused by the flow in the capillary.

In order to apply the Laplace equation to characterise the pore structure of these networks, and to use the Lucas-Washburn equation to describe the rate of liquid penetration into these systems, it is necessary to make a series of explicit and implicit assumptions. The six explicit assumptions are:

- a) The wet pore radii are the same as the corresponding dry radii.
- b) The liquid comes from an unlimited reservoir.
- c) The flow is only in one direction.
- d) The contact angle θ between mercury and the pore walls is 140° (a traditional value used in the absence of more precise measurements), and the contact angle of air displacing hexadecane is 180° (i.e. air is entirely non-wetting when displacing fully wetting hexadecane). In practice, the pore walls within filled sheets will not be perfectly smooth and will probably be rougher than the surface. The contact angle of mercury, θ , on a rough porous surface is generally greater than that on a microscopically smooth surface. A review of some roughness theories is given by Good and Mikhail (25).
- e) The interfacial tension γ at the interface between the mercury, the fibre or pigment, and the vacuum or residual air displaced by the mercury, is assumed to be the traditional value of 0.48 Nm⁻¹, again used in the absence of specific measurements. For hexadecane, $\gamma = 32 \text{ mN} \cdot \text{m}^{-1}$. (Assuming a contact angle of 140°, and an interfacial tension of 0.48 Nm⁻¹, equation (1) predicts that mercury will intrude cylindrical pores of diameter 0.0072 μ m at the upper experimental pressure limit of 207 MPa.)
- f) In comparison to the uncertainties in θ and γ , effects due to the instrument-grade mercury taking up impurities were safely assumed to be negligible, as was the Tolman effect (26) which is only evident in micropores (< 2 nm).

Most workers using the Laplace and Lucas-Washburn equations (including Yamasaki, below) rely on a major implicit assumption, namely that all the pores act separately and all are completely accessible for intrusion or drainage at all pressures. Correspondingly, it is assumed that the pore size distribution can be obtained by finding the first derivative (i.e. slope) of an intrusion or drainage curve. No account is made of the three dimensional interconnectivity of the network, which in reality causes the *shielding* or *shadowing* of large voids by the smaller connecting voids which surround them.

Yamasaki model.

In a model recently published by Yamasaki (27), the pore size distribution is taken into account and the Lucas - Washburn equation is then applied to all pore sizes individually and summed to simulate the absorption. The working equation is:

$$V(t) = K_{\rm r} + \Sigma (V_{\rm Ti}) + (\gamma t/2\eta)^{1/2} / (\xi d) \Sigma (V_{\rm Ti} r_{\rm i}^{1/2})$$
(2)

where

V(t) is the volume of liquid transferred to the sheet at time t;

- K_r is the roughness factor, i.e. the surface pores of the sheet which represent the liquid transferred to the sheet without any capillary action;
- $\Sigma(V_{\text{Ti}})$ is the sum of all pores filled with liquid during the absorption and which hence no longer contribute to the time dependence of the absorption but naturally contribute to the absolute volume of absorbed liquid;
- γ is the surface tension of the absorbing liquid;
- d is the effective thickness of the sheet;
- ξ is the tortuosity, which is defined as the ratio between the actual penetration distance and the effective thickness of the sheet, i.e. the actual penetration distance (ξd);
- η is the viscosity of the absorbing liquid, and
- $V_{\rm Ti}$ is the total volume of capillaries of the radius r_i per unit area.

Incorporated into the equation is the assumption that $\theta = 0^\circ$, and therefore $\cos \theta = 1$. In the present work, it was also assumed that the roughness factor, K_r , was zero.

Yamasaki's model suggests that all of the pores contribute to the time dependence of liquid absorption as long as they are not saturated. Once the pores are saturated they are transferred to the $\Sigma(V_{\rm Ti})$ term. In the present work this model was set up as an Excel spreadsheet, and the liquid transfer integrated with respect to time. After each integration, the total volume of absorbed liquid in each capillary was compared to the maximum liquid volume available in the sample described as the maximum from the porosimetry measurements.

Pore-Cor model.

In the Pore-Cor model, the void space within a porous medium is regarded as an array of larger *pores* connected by smaller *throats*. The void space is simulated with a network of nodes positioned at the centre of each pore, connected by arcs along the line of each throat. The complete network comprises a series of identical 3-dimensional unit cells. repeating indefinitely in each Cartesian direction x, y and z. The sample is divided into identical unit cells each containing 1000 nodes in a 10 x 10 x 10 array equally spaced in the Cartesian coordinates. The void volume in the unit cell consists of up to 1000 cubic pores centred on the nodes. Each pore is connected to a maximum of six cylindrical throats which lie along the line of the arcs in the positive and negative x, y, and zdirections. The number of throats connected to a particular pore is referred to as the coordination number and the arithmetic mean of this quantity over the whole unit cell is referred to as the connectivity. For the calculation of the intrusion and extrusion of a nonwetting fluid, and the permeability to a wetting fluid, the non-wetting fluid is applied at the top face $(z = l_{cell})$ in the -z direction for each repeating unit cell. Thus intrusion and permeability both apply to an infinite sheet of thickness l_{cell} , although in practice the permeability is the same as it would be for a three dimensionally infinite sample of the modelled substance

The throat size distribution consists of 100 different sizes spread log / linearly between the minimum and maximum diameters calculated by applying the Laplace equation to the experimental data. The term *throat skew* is defined as being the percentage of throats of the smallest of these 100 diameters. These throats are randomly positioned within the unit cell. A pore is then assigned to each node that has at least one throat connected to it. For a *pore skew* of 1, the pore size is set equal to the diameter of the largest throat reaching that node. Larger values of pore skew give correspondingly larger values of the ratio of pore size to largest-throat diameter, although the pore size distribution is truncated at the size of the largest throat diameter.

Mercury intrusion is simulated by means of an invasion percolation algorithm which calculates the fraction of pore volume occupied at a series of increasing, static mercury pressures. The algorithm takes into account the shielding (or shadowing) of large pores by adjoining small throats. The simulated intrusion curve is fitted to the experimental curve by altering the throat skew and connectivity (28, 29). Finally, the row spacing of the matrix, which has a negligible effect on the intrusion curve, is adjusted so that the porosity of the simulated network equals that of the experimental sample.

Garboczi (30), has suggested that the two main limitations of using a percolation algorithm based on the Laplace equation are, (i) that the throats are all considered to be cylindrical, and (ii) that the mapping of the effective network derived from the mercury porosimetry curve is not the same as the real network, Kent and Lyne (6).

Once the three-dimensional void structure has been simulated, its flow capacity is calculated according to the equation:

$$\left(\frac{\mathrm{d}V}{\mathrm{d}t}\right)_{\mathrm{cdl},-z} = -\frac{\pi}{8\mu} \Omega \left(\frac{r_{\mathrm{nuber}}}{l_{\mathrm{nuber}}}\right)_{\mathrm{cdl}} \frac{\delta P}{\beta}$$
(3)

The term $(r_{\text{tubes}}^4 / l_{\text{tubes}})$ takes into account the flow capacity through individual porethroat-pore arcs. Ω is Operational Research operator which, on the basis of the individual arc capacities, calculates the maximal flow capacity of the whole unit cell, Matthews (31). In this study permeability factors were calculated for air at one atmosphere pressure (28, 29). In general, the permeability factors have been found to differ from experimental absolute permeabilities, with the difference between the absolute and experimental values increasing by successive orders of magnitude as the complexity of the network increases. However, in general they follow the correct experimental trends.

EXPERIMENTAL

Mercury porosimetry of paper.

The mercury intrusion curve of a porous sample comprises measurements of the volume of mercury intruded, V, against applied pressure. Corrections are applied to allow for the expansion and contraction of the sample chamber, penetrometer and mercury, (Gane (32)). The applied pressure is then converted to a throat diameter using the Laplace equation. The intrusion curve is typically sigmoid in shape and traditionally it has been assumed that the distribution of throat sizes (not distinguished from pore sizes) can be equated to the first derivative of an intrusion curve dV / dd. This results in a distribution which has a peak at the point on the intrusion curve which has the highest gradient i.e. the point of inflection. The Lucas-Washburn derived throat diameter at this point is often described as the characteristic

throat diameter. Porosimeter control software usually incorporates the first derivative assumption and such software sometimes extends this assumption to derive a particle size distribution for the solid. The assumption is implicit throughout all the analyses of the LADA, Bristow and liquid porosimetry results in this work. However, the use of the first derivative is only valid for a porous solid which comprises a bundle of unconnected capillary tubes, which can be tortuous, but which must be of constant diameter along their length. The Pore-Cor analysis avoids the use of the firstderivative assumption, but remains subject to the Lucas-Washburn assumptions described earlier, and others described later.

To measure the pore structure of a porous material using mercury porosimetry, the sample initially needs to be fully evacuated. Ideally, it should then be surrounded with mercury with no applied pressure. The mercury pressure is then gradually increased to probe smaller and smaller pores. In practice, mercury is a very dense liquid, and enters the largest external pores of its own accord even though, nominally at least, there is no applied pressure. The other problem is that its penetration characteristics at the surface are likely to imply a different threshold between surface roughness and internal pore space. Hence mercury porosimetry is not a good technique at the lowest applied pressures which correspond to the largest void sizes. The failure of mercury to correctly probe the largest pores is obviously a limitation to the analysis of uncoated papers. It is natural to have large pores in uncoated paper, since the building block, i.e. the fibres, have a diameter of approximately 20 μ m. When it comes to interaction with different liquids, these large pores are very important since the liquids absorb faster in the larger pores as described in the Lucas-Washburn equation. This characteristic will be discussed in detail in a later part of this paper.

Liquid porosimetry using hexadecane and water probe liquids.

In order to determine the pores in the micrometer range it is necessary to have a technique which is complementary to the mercury porosimetry. Miller and Tyomkin (32) have published a liquid extrusion technique which can be used for this purpose. The method is normally referred to as liquid porosimetry even though the other technique also uses a liquid, namely mercury. The apparatus used was a TRI Autoporosimeter which measured gravimetrically the liquid extruded from a pre-saturated paper sample at different, well determined, air pressures. The gas pressure in the sample chamber is increased in steps, causing liquid to flow out of the sample through the largest pores first. A thermocouple sensor is installed in the sample

chamber to monitor temperature changes. Even small temperature fluctuations can produce changes in density of the liquid which would cause errors in the evaluation of the pore volume. The weight of liquid removed is monitored by a top-loading recording balance. In this way, each level of applied pressure (which determines the largest effective pore size that remains filled) is related to an increment of liquid mass. The readout of the thermocouple is fed to the computer and the recorded liquid mass changes are automatically corrected for any observed temperature drift. By applying the Laplace equation, (1), it is possible to create pore volume distribution curves from these data.

Draining the pores in this step-wise manner requires very small increases in pressure over a narrow range which is slightly above atmospheric pressure. To achieve this, the chamber is pressurised by means of a computer controlled, reversible motor driven piston / cylinder arrangement which can produce the required changes in pressure to cover a pore diameter range from 6 μ m to 1000 μ m. The pressure is monitored by one of two transducers (a pair are used to maintain sufficient accuracy at both low and high pressures): the signal is fed to the computer which, through feedback logic, adjusts the piston position to set the target pressure almost instantly. By monitoring the balance output the computer ensures that equilibrium is reached prior to further pressurisation. This process is repeated for the whole pressure range.

The TRI Autoporosimeter is shown in Figure 1:



Figure 1: Basic arrangement of liquid porosimeter.

The porous membrane on which the sample rests contains $0.44 \,\mu\text{m}$ diameter pores and there is significant void space between it and the adjacent sheets. To prevent this effect dominating the results, several sheets had to be studied and the effect of the substrate subtracted, as discussed in the results section.

A powerful feature of the liquid porosimetry technique is that sheets can be characterised by the displacement of wetting fluids which either do or do not cause swelling. By comparing measurements with water (swelling) and hexadecane (nonswelling), it is possible to determine the expansion of the sheets on exposure to water and the pore size range in which this expansion takes place. The expansion is mostly due to a release of the bonds between the fibres but also to a minor degree due to the swelling of the fibres themselves.

By combining the liquid and mercury porosimetry data it is possible to get a more complete picture of the pore structure of the paper under investigation. The procedure for doing this is described later in this paper.

Absorption and permeability testing.

The absorption properties of the sheets were tested by two different methods, the Bristow absorption tester and a new Liquid Air Displacement Analyser, LADA. The Bristow absorption tester has been described by many authors, e.g. Lyne (33), and will not be described further here. In order to be able to detect the "track"-length of the liquid in this equipment, deionized water was mixed with methylviolet dye to give a final concentration of $0.2 \text{ g.} \text{I}^{-1}$. The surface tension of the solution, determined with the de-Nouy ring method, was 69 mN.m⁻¹. In these experiments both the wire side and the top side of the sheets were tested.

A detailed description of the LADA equipment has been given recently by Miller (34). In this equipment the spontaneous absorption of liquid into a paper sample is determined by monitoring the buoyancy force of a sample in a specimen holder as liquid is absorbed into the paper. The absorption into 31 mm diameter circular samples was investigated. Ten samples of each sheet were measured and averaged. Deionized water, surface tension 71 mN.m⁻¹, was used in all experiments. The advantage of the LADA equipment is that the liquid is applied in a well-defined manner to the sheet, from an unlimited reservoir, and there are no obstructions to the flow from the equipment itself.

Air permeability can be measured with a 'Gurley Densometer'. It is evaluated by obtaining the time taken for a given volume of air to flow through a specimen of given dimensions under standard conditions of pressure, pressure difference, temperature and relative humidity. The permeabilities can be expressed as flow time per 100 ml of air, or as microDarcies, where $1\mu D = 9.87 \times 10^{-13} \text{ m}^2$.

Electron microscopy.

An Environmental Scanning Electron Microscope (ESEM) from Electroscan, Boston, USA, was used to produce images of the surface and sections through each sample at different humidities. The major advantage of this technique is that the sheets need no gold coverage since the atmosphere around the sample can be varied from almost completely dry to completely water saturated.

In the present investigation images were taken at 50% relative humidity (RH) of sheets which had and had not been exposed to an atmosphere at 98% to 99% RH. The sheets which were exposed to the higher humidity were conditioned at 50% RH before new images were taken. In order to avoid radiolysis the sheets were not kept in the electron beam during this treatment.

RESULTS

Physical properties of the papers.

The paper was analysed and found to contain 18 % chemical pulp and 82 % mechanical pulp. The paper had a relatively high kaolin filler content of 30 wt%. In this work, the five selected samples were, the uncalendered paper, a paper supercalendered at 800 m.min⁻¹, with and without steam pretreatment, and soft nip calendered papers calendered at 400 m.min⁻¹ again with and without steam pretreatment. The physical, optical and printing properties of the paper samples were measured using a range of standard procedures. The z-direction thicknesses (calipers) of the papers were measured using optical microscopy and image analysis. Their mean calipers are listed in Table 1 overleaf.

The substance values of the sheets were nominally 53 g.m⁻². The respective densities and proportions of the solid materials (e.g. fibre and filler) were known and this gave a solid phase density of 1.723 g.cm⁻³ and a solid phase volume of 0.580 cm³.g⁻¹. This information was sufficient to calculate the sheet porosities. As expected, the uncalendered paper sheet was the most porous and the sheets calendered after steam pretreatment had lower porosity than their equivalents that had been calendered without steam pretreatment. The conventional optical and printing properties of all the paper samples in this study were measured according to standard TAPPI test procedures and the results are also listed in Table 1.

It can be seen from the table that calendering the papers increased the sheet gloss and lowered the brightness and opacity. The improvement in sheet gloss is due to improved sheet smoothness as measured by a Parker Printsurf apparatus, and the decrease in sheet brightness is due to reduction in light scattering ability. Supercalendering caused the paper to have the largest drop in brightness and resulted in the lowest light scattering ability. The decrease in opacity is due to the thinning of the papers on compression.

The Gurley Densometer permeability values can be seen to be very sensitive to the degree of calendering and the effect of steam pretreatment that the sheet had experienced; a high degree of calendering resulted in a sheet of low permeability.

	Uncalendered	Softnip	Softnip	Super	Super calendered
	paper	calendered	calendered	calendered	no steam
		steam	no steam	steam	
Mean caliper / µm	66	51	58	46	54
Substance / g.m ⁻²	53	54	53	53	52
Gloss	4	34	29	35	26
Brightness	70.1	67.7	68.0	66.7	68.3
Opacity	94.0	92.9	93.2	91.9	93.0
Light scatter	700	600	620	530	610
"S"/ cm ² .g ⁻¹					
Light absorption	26.4	27.5	28.5	28.3	28.1
"k" / cm².g ⁻¹					
Smoothness / µm	5.9	1.3	1.4	1.3	1.5
Sheet density / g.cm ⁻³	0.808	1.053	0.910	1.131	0.975
Sheet volume / cm ³ .g ⁻¹	1.238	0.950	1.099	0.884	1.025
Porosity / %	53.1	38.9	47.2	34.4	43.4
Gurley Permeability					
seconds per 100mls	60	308	240	368	276
microDarcies (µD)	2357	357	522	271	425

Table 1: Physical properties

Mercury Porosimetry Results

The mercury porosimetry curves for the papers are shown in Figure 2. They cover a wide range of throat diameters extending over the range of 200 μ m down to 0.007 μ m. It was assumed, from the ESEM micrographs, that the pore volume attributed to throat diameters greater than 40 μ m resulted from sheet roughness (e.g. edge effects) rather than pore volume attributed to the bulk of the sheet. Hence the characteristic (d_{50}) diameters were calculated as the 50 % volume between the throat diameters of 40 μ m to 0.007 μ m. The mercury porosimetry data shows that the uncalendered paper has the highest pore volume in the 200 μ m to 40 μ m throat diameter region, i.e. the sheet surface is the roughest, in agreement with the smoothness results listed in Table 1. There is a decrease in the pore volume and a shift toward finer pores for the calendered sheets. The porosimetry curve for the sheet supercalendered without steam pretreatment is almost coincident with that of the sheets calendered by the soft nip calender. This indicates that without steam pretreatment it is possible to match the porous nature of the sheet by both

calendering techniques. This finding has industrial significance due to the growing trend towards on-line soft nip calendering rather than off-line supercalendering. The use of steam pretreatment prior to supercalendering generated the most dense (least porous) sheet.



Figure 2: Mercury porosimetry data of papers.

Liquid Porosimetry Results.

Ideally, liquid porosimetry should provide an unambiguous measure of hexadecane drainage for a particular paper sample. However, various problems arise. The first is that a certain volume is created between the sheet and the membrane. An attempt was made to correct for this by assuming that this created volume behaved simply as a single sheet, and that its weight disappeared when sample sheets were placed on it. However, this proved to be too crude a correction, giving negative drainage values. Therefore, it was necessary to extrapolate the drainage of the multi-sheet samples to a zero-sheet drainage. The volume between the membrane and the sheet was then assigned an effective sheet-weight, such that its drainage then agreed with the zero-sheet drainage. Having carried out this procedure, the "artificial" volume created

between the paper and the membrane was then subtracted from the multi-sheet drainage curves, to give the net drainage of the paper sheets on their own. The drainage was then normalised by sheet weight, in $ml.g^{-1}$, Figure 3.



Figure 3: Wetting fluid drainage of samples containing varying numbers of sheets

It can be seen that many of the drainage points diverge from one to two sheets, which is attributed to the fact that the membrane drainage dominates the small amount of drainage from the single sheet sample. To eliminate this effect entirely, it is wise to use at least three sheets. For high numbers of sheets, the normalised drainage decreases, which is attributed to fluids being trapped in the inter-sheet spaces. Therefore, three sheets was taken to be representative for all the samples.

Figure 4 shows the liquid porosimetry curves for all the 3-sheet samples. In line with the mercury porosimetry data, the uncalendered sheet was the most porous and there was a step-wise decrease in porosity as the calendering speed of the soft calender was reduced. The supercalendered sheet had the lowest porosity. The curves on the graph do not reach zero volume because there is still some hexadecane probe liquid



Figure 4: Liquid porosimetry data of papers.

Combination of mercury porosimetry and liquid porosimetry data

The first stage in combining mercury and liquid porosimetry is to express the liquid extrusion as air intrusion, Figure 5.



Figure 5: Liquid porosimetric data of uncalendered paper.

The next stage is to select the most reliable parts of the two intrusion curves for each sample, exemplified for uncalendered in Figure 6. To do this, one bears in mind the previous discussions that mercury porosimetry is unreliable for large pores (> 10 mm) and liquid porosimetry mainly probes sample edge effects above 100 µm. The truncation of the unreliable regions gives the curves shown in Figure 7. They are then joined, on the assumption that in the overlap region, liquid porosimetry is most reliable. The assumptions about where to truncate the curves is somewhat arbitrary. and the final combined curve was therefore checked to ensure that there were the correct contributions to the overall porosity from the different void size ranges. For example, by excluding the pore volumes in the combined curve attributed to throats greater than 40 µm throat diameter, a value of 53.1 % porosity was calculated. This was in good agreement with the value measured by mercury porosimetry in which the pore volume attributed to large pores were ignored. This combined porosimetric data, Figure 9, was used for the adsorption simulations with the Yamasaki model, and also in the Pore-Cor simulations.



Figure 6: Intrusion data from both porosimetric techniques, uncalendered paper.



Figure 7: Truncated porosimetric data for uncalendered paper.



Figure 8: Combination of porosimetry data.

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Absorption of liquids into the different papers.

As mentioned earlier in the experimental section the papers were tested with both the Bristow tester and the LADA technique in order to characterise how the papers absorb water. The results are shown in Figures 9 and 10 respectively. As can be seen, the uncalendered sheet absorbs water fastest in both methods, followed by the sheets calendered without steam, whilst the sheets calendered with steam show the slowest absorption. It should be noted that in the Bristow absorption there is no difference between the soft nip calendered sheets with and without steam application.



Figure 9: Absorption of water, in cm^3/g , into the papers as determined with the Bristow absorption tester.



Figure 10: Absorption of water, in cm^3/g , into the papers as determined with the LADA absorption tester.

Another difference between the papers is the absolute volumes found in the absorption testing. The volumes in the LADA testing are much lower than those in the Bristow absorption tester. There are probably several factors which cause the discrepancy between the two methods. However, the LADA values are closer to the porosity values measured by the combined porosimetry techniques, Figure 8. This suggests that the Bristow method may be measuring a different, non-bulk property, such as the surface roughness and/or near-surface porosity of the sheets.

To make an even more thorough comparison between the two methods, the Yamasaki model, equation (2), was used to simulate the absorption of water in the different sheets, and the simulated values compared with experiment. Some of the results are shown in Figure 11, namely the LADA absorption values for the uncalendered sheet and the SC sheet, with steam treatment, together with the simulated absorption values. The values for the properties of pure water at 20 $^{\circ}$ C were used in the calculation, i.e. γ = 72 mN.m⁻¹, η =1x10⁻³ N.s.m⁻², together with the calipers shown in Table 1 and the combined porosimetry curves shown in Figure 8. A tortuosity factor of 6 was chosen for the uncalendered sheet, partly arbitrarily and

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partly based on the work by Yamasaki (27), and the fortuosity of the SC sheet was calculated in direct relation to the change in thickness from the uncalendered sheet to the SC sheet to be 8.5 (i.e. 6x66.0/46.5).



Figure 11: Comparison between the actually measured absorption, with the LADA equipment, and the simulated absorbed values with the Yamasaki model.

There is good qualitative agreement between the simulated absorption and the absorption measured with the LADA absorption tester (Figure 11), giving further support to the idea that the LADA adsorption is a measure of bulk rather than surface, pore structure.

Another result which can be seen in Figure 11 is that the deviation between the simulated values and the measured values becomes larger at longer absorption times and also larger for the calendered sheet than the uncalendered sheet. One explanation for this deviation could be that the wet structure is not the same as the dry structure, because the sheets expand upon wetting (Skowronski (14)). This would mean that

the wet sheets can hold considerably more water than the dry sheets. In order to test this the sheets were tested with the liquid porosimeter using water and a surfactant to reveal the wet, swollen void structures of the paper samples. In figures 12 to 14, the cumulative volumes for pores larger than 6 mm in diameter are compared with the dry, un-swollen structures measured with hexadecanes and shown previously in Figure 4. As can be seen, there is a considerable expansion for the uncalendered sheet and for the soft nip calendered sheets, but only a limited expansion for the supercalendered sheets. This indicates that the supercalendering procedure gives a permanent compaction of the sheets for this pore size range. By contrast, the soft nip calendering gives only a temporary compaction of the sheets, which almost regain their original volume when wet with water.



Figure 12: Wet and dry cumulative volume of the uncalendered sheet.



Figure 13: Wet and dry cumulative volume of the soft calendered sheet, with and without steam treatment.



Figure 14: Wet and dry cumulative volume of the supercalendered sheet, with and without steam treatment.

The void structure less than 6mm in diameter contains immobile fluid, and is known as the 'gel volume'. To measure this volume, a valve between the measuring chamber and the balance (not shown in Figure 1) is closed before the pressure in the chamber is released. The sheet with liquid remaining in pores smaller than 6 μ m in diameter is then weighed, and the amount of remaining liquid calculated by subtracting the dry sheet weight. As is shown in Figure 15, there is a large expansion for all sheets in this pore size range and the largest relative volume expansion can be found for the supercalendered sheets, which showed the smallest expansion in the upper size range. The difference between the soft calendering and supercalendering, and the ability of the pressure impulse to soften the mechanical pulp fibres in the sheet. The higher pressure impulse does not affect the bulk voidage very greatly, Figure 14, but does crush the gel volume, Figure 15, which re-expands on wetting and swelling of the fibres.



Figure 15: Wet and dry cumulative gel-volume, i.e. volume in pores smaller 6 μ m in diameter.

Another advantage of the Yamasaki model (27), so far not yet mentioned, is that the filling of the different pores can be shown at different times. As an example the results from the uncalendered sheet simulations are shown in Figure 16. It can be seen that after around 1 second the larger pores are already almost filled, whereas the pores in the smaller size ranges are still absorbing.



Figure 16: Simulation of the time-dependence of water absorption in the uncalendered sheet, using the Yamasaki model and the combined porosimetry data.

There is thus a clear relationship between pore size distribution and the timedependence of water absorption. A qualitative prediction of this relationship is therefore possible using the Yamasaki model, and the dry and wet pore-size distribution. If a quantitative relationship between the wet and dry pore size distribution could be determined, and if the contact angle and tortuosity factor were exactly determined, this work has shown that it would be possible to predict the absorption of different liquids into paper in detail using an extended Yamasaki model.

Electron microscopy.

The volume change detected with the PVD equipment by using different liquids was also detected by measurements with the ESEM. The sheets were exposed to almost saturated water vapour, before reconditioning to 50 % RH. The results from these measurements for the uncalendered sheet, and the supercalendered sheet with steam treatment, are shown in Figure 17 and 18 respectively. All the scale bars are 50 microns long.



Figure 17: ESEM pictures of the dry and wet uncalendered sheet, shown left and right respectively



Figure 18: ESEM pictures of the dry and wet supercalendered sheet, with steam treatment, shown left and right respectively

These measurements suggest that the deviation between simulated absorption values and measured absorption values, Figure 11, is most probably related to the structure change upon absorption.

Simulated properties of paper systems.

The combined intrusion curves, shown in Figure 8, were also simulated using the Pore-Cor software. The parameters which generated the simulated curves are shown in Table 2 (conn. = connectivity). The experimental and simulated porosities were identical to within 0.1%. Also shown are the absolute permeability factors (equation (3)) which resulted from the structures.

Sample Reference	Minimum throat diameter / µm	Max. throat diameter / μm	Throat skew	Pore skew	Conn	Porosity / %	Permeability Factor
Uncalendered	0.007	200	-0.9	2.5	2.9	53.1	4.45x10 ⁻²
Softnip							
calendered							
with steam	0.007	200	0.60	2.4	2.9	38.9	3.83x10 ⁻⁶
without steam	0.007	200	0.57	3.4	2.9	47.2	1.16x10 ⁻⁵
Supercalendered							
with steam	0.007	200	0.42	1.9	2.9	34.4	9.93x10 ⁻⁵
without steam	0.007	200	0.45	2.9	2.9	43.4	5.62×10^{-3}

Table 2: Simulated data for paper systems



Figure 19: Examples of experimental and simulated intrusion curves

The simulation of two of the combined porosimetry curves is shown in Figure 19. The Pore-Cor software assumes that a non-wetting fluid intrusion curve will be sigmoid in shape, as predicted by 3-dimensional percolation theory, and hence the optimum simulated curves do not fit the experimental curves over their entire length. The simulation generates permeability factors which, with one exception, track the permeability values measured experimentally using the Gurley densometer.



Figure 20: Pore and throat size distribution for basepaper and supercalendered paper with steam.

The changes in pore and throat size distribution on calendering are clearly shown in Figure 20, illustrated for the basepaper and supercalendered sheet with steam. Both the pores and throat sizes are substantially reduced, as shown experimentally in Figures 17 and 18. Figure 21 shows the Pore-Cor three-dimensional structure of the base-paper, and Figure 22 that of the supercalendered paper with steam, again clearly showing the reductions in pore and throat sizes.



Figure 21: Simulated void structure of the base paper



Figure 22: Simulated void structure of the calendered paper with steam.

The main advantages of the Pore-Cor model over the Yamasaki and other models are:

- a) The shadowing or shielding of large pores is taken into account.
- b) An explicit geometry of the void space is derived, on which the calculation of all other properties is based.
- c) Other properties of the networks are revealed in this case, for example, the modelling reveals that as the network is compressed by calendering, its connectivity does not change.
- d) The void-space model can be used for the investigation of other effects, such as the trapping of non-wetting fluids, the reduction in permeability caused by compression, and the inclusion of fine particles of fibre or colloid within the voids.

The main limitations of the Pore-Cor model are:

- a) The simulation does not fit the experimental intrusion curves very well. At the present time, it is not possible to judge the relative contributions to this discrepancy of weaknesses in the experimental data, and weaknesses in the modelling itself. With regard to the experimental data, the combined porosimetry curves do not have the normal sigmoidal shape because of their formation by the direct combination of two porosimetric techniques. With regard to the modelling, the limitations lie mainly in the simplified geometry of the unit cell, and include the specific limitations described in b) and c) below.
- b) The void-space geometry is simplified to an array of cubes and cylinders, and although the sizes of the voids reduce on calendering, their shapes do not change as they should.
- c) The unit cells are just over 2mm in size much larger than the samples themselves. This is because the largest pores, which give the model the correct fairly high porosity, space out the entire unit cell. These large pores are largely an artefact of the modelling, and it is the smaller pores and throats in Figures 21 and 22, which are difficult to see, which are the most important. The changes in pore and throat size distribution are clearer to see in Figure 20, where the large pores at the right-hand end of the pore size distributions can easily be ignored. The solution to this problem would be development of the Pore-Cor model such that the correct porosity could be achieved by packing smaller pores more efficiently, rather than having their positions fixed to equally spaced positions in Cartesian coordinates and enlarging them with the pore-skew parameter.

CONCLUSIONS

In the present work we have applied a variety of tests and void space modelling techniques to a series of five paper samples. The absorption properties of the sheets were determined both by using the well known Bristow equipment and newly-developed equipment for determining liquid absorption by fibrous sheets based on Liquid / Air Displacement Analysis (LADA).

The mercury porosimetry data and the liquid porosimetry data were combined to yield a complete pore volume distribution curve for the sheet structure. These data were then used in the Yamasaki absorption theory to simulate absorption, and were compared with the measured absorption values. These results show that the absorption can be simulated with a knowledge of the pore volume distribution curve and basic properties of the absorbed liquid. The Yamasaki simulation also shows that the large pores dominate the liquid absorption at short contact times (<1s), whereas the smaller pores dominate the absorption at larger contact times. The combined porosimetry data were also used for the Pore-Cor model. This model yielded simplified 3-D geometric representations of the sheets which matched the experimentally determined porosities and pore size distributions. With the exception of one sample, the permeabilities calculated for the simulated Pore-Cor structures tracked the Gurley permeability values.

Results from the investigation with liquid porosimetry using water and hexadecane probe liquids show that there is considerable sheet expansion when the sheets are exposed to water. Undoubtedly this will lead to a change in the absorption process when the sheets are in contact with moisture. The shape of the absorption curves in the Bristow test equipment also indicate that this expansion will affect the absorption process. The absorption after around 1 s in the LADA absorption measurements comes from the smaller pores whereas the larger part of the absorption at times below 1 s emanates from the larger pores. Naturally the influence of the different pores will be determined by the relative amount of the small and large pores of the total pore volume available in the sheet. There was a large expansion for all sheets in the fine pore size range and the largest relative volume expansion can be found for the supercalendered sheets. This means that all sheets show a large expansion upon wetting even if the supercalendered sheets only showed a minor expansion in the larger pore size range. The reason for this difference between the soft calendering and supercalendering is probably due to the difference between the pressure impulse

during calendering and the ability of the pressure impulse to soften the mechanical pulp fibres in the sheet. Obviously it is not possible to avoid an expansion in the smaller pore size range even with a higher pressure impulse. This volume change was also detected by ESEM measurements.

The relationship between the pore structure and water absorption show that the Yamasaki model may be used to predict qualitatively the absorption of water into the sample sheets. A quantitative relationship would require accurate values of the contact angle and tortuosity factor. The contact angle could, in principle, be found experimentally. The exact physical meaning of the tortuosity factor is unclear in the context of the implicit complete-accessibility assumption described earlier. However, the tortuosity factor can be used to provide some correction to this accessibility assumption, and optimizing its value could therefore generate a usable and useful model. In particular, such an extended Yamasaki model could be used to provide a relationship between the wet and dry pore size distribution, and to predict the absorption of different liquids into paper.

The Pore-Cor model gives a clear indication of the effect of calendering, in terms of the change in the sizes of the voids, and the lack of change of connectivity of the void network, but does not have the capability yet to model the changes in shape. The difficulties of modelling discussed earlier lead to the conclusion that the pore and throat size distribution graph, Figure 20, is a truer indication of the effect of calendering than the 3-D structures in Figures 21 and 22. Despite the shortcomings of Pore-Cor, it has the advantage that the limitations of the model, and possibly the experimental data, are immediately obvious. Thus, though imperfect, the model can be used with wise caution, with clear directions for development. The extension of the pore and throat size distributions in Figure 20 to a time dependency should in principle be more reliable than for the Yamasaki model, because the pore and throat size distributions have allowed for the shielding / shadowing effects discussed earlier.

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Transcription of Discussion

Investigation of the pore structure of paper by novel porosimetric techniques: application to super- and soft-nip finishing

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"Errata"

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To bring the text and the reference list in this paper into agreement the reference numbers in the text greater than including reference 32 need to be increased by 1, i.e. 32 becomes 33 in the text.

The first line on p1381 of the proceedings states "6mm in diameter" and this should be "6 μm in diameter"

Sven Lohmander, Research Engineer, STFI, Sweden

You use cylinders to describe the throats in your model which means that in one plane you have a spherical cross section which in turn means that you can only govern the size of the throats but not the shape. Don't you think it's possible to use an elliptical cross section to be able to govern both the shape and the size to get a better fitting of your model to experimental data?

John Kettle

I think that is one of the points I have raised when I described the limitations of the computer model. We need to be able to change the shape and size of pores and throats after calendering. In this case the cylindrical cross section would then become more elliptical and that would then probably make a better fit between simulation and experiment.

Sven Lohmander

So you think then that it's possible because that would require an additional parameter which would cause a further complication in your model.

John Kettle

I should refer that question to Peter Matthews who's done all the programming work, but it should be possible.

Dr Richard Bown, European Technical Director, ECC, UK

This may be an artifact in your data. When you calender the paper the pore volume goes down as expected, but the pore size distribution doesn't seem to change. This may well be connected to the last question in that the pores change shape in a way that changes their volume but does not influence their apparent radius. I wondered if you had an opinion on that?

John Kettle

Yes, I must admit I did notice that effect. It isn't unique and I've seen it with other papers. There is a slight movement of the pore size distribution after calendering but it is not clear on these curves and it isn't as great as I might have expected. In my thesis work I studied dried coating colour layers as well as papers and you actually do see a more pronounced effect depending on the pigments or formulation used.

Alfred Nissan, Retired

I perhaps should not make this comment because last time I made a comment on fluid mechanics I was hauled over the coals 45 years later. I hope you won't hold it against me.

John Kettle

If we're both here in 40 years time it'll be good!

Alfred Nissan

The use of the Washburn equation is of course well established. It is an accurate equation but not in the first fraction of a second. In many operations, both in papermaking and particularly in printing and converting and so on, then absorption is in less than half a second. During that time you start from zero velocity. The velocity distribution across the capillary is uniform but the Washburn equation is for parabolic distribution of velocity which has to develop. There is a finite time and finite length in which the boundary layer has to build from uniform velocity to a non-uniform but parabolic. During that time it is not the viscosity that is controlling, it is a mixture, but in the beginning it is purely the density which is controlling. Therefore if you are dealing with the first fraction of a second, and in many operations that is the position, one has to be careful with the Washburn equation and not use it without corrections for the entry length. But, beyond that, of course, it is <u>'the</u>' equation, it is as good as you can get. Thank you very much.

John Kettle

I agree care has to be taken when using the Washburn equation and I have also described in this paper the assumptions which rightly or wrongly have to be made.