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SWELLING DURING THE PENETRATION OF AQUEOUS LIQUIDS INTO PAPER

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Synopsis The present state of knowledge concerning the transudation of aqueous liquids into paper is reviewed. Theories for the swelling of cellulose and cellulose fibres are examined and related to the swelling of a porous web of paper. A method of measuring, simultaneously, the penetration and resultant swelling of the sheet by aqueous solutions is described. The results of the above measurements for water, water containing a wetting agent, starch solution, cuprammonium hydroxide solution and a glycerine/water mixture are reported. It is shown that the swelling is an integral part of the penetration process. Deviations from the Lucas–Washburn equation are due to the neglect in the penetration equation of the swelling of the sheet. Apparent diffusion coefficients are calculated from the swelling data and it is shown that swelling is controlled by a diffusion mechanism.

Introduction

A STUDY of the penetration of water into paper covers three areas of interest. These are water–fibre interaction, description of the porous structure of the web and flow of water through the web. In a recent review of this subject Hoyland and Field(1–5) have adopted the term transudation to define the complete penetration of water through a piece of paper. In the following, an attempt is made to examine the factors involved in the transudation of water into paper and the associated swelling of the paper web. A method of measuring, simultaneously, the penetration of aqueous liquids into paper and the swelling is described. The results obtained using this method are examined with a view to elucidating the mechanisms involved.

Penetration of liquids into paper

THE nature of the porous structure of paper, with regard to the transudation of water through paper, is of considerable importance, since an understanding of paper structure would enable direct application of the laws

Under the chairmanship of Prof. M. Judt governing fluid flow to be made. The structure of a paper web is sufficiently complex that problems are encountered in its mathematical description and even in defining such concepts as porosity. The pore volume is arranged within the sheet in a totally irregular way. Some pores may connect only with one surface, termed recesses, and will not contribute to liquid flow through the sheet. Space can remain within the lumen and may be completely enclosed. Space within the sheet may also be completely surrounded by fibre. Such spaces which are not connected in any way to the outside of the sheet are called voids and they cannot take place in the free flow of liquid in the structure. The pores available for penetration must connect with both surfaces and may be highly-branched and interconnected within the structure. Another factor influencing the pore structure of paper is moisture content. Fibre dimensions vary with moisture content and in general fibres swell on increasing moisture content. The pore size distribution of papers at different moisture contents has been measured and it has been shown that the mean pore size increases over the range 0 to 10 per cent moisture content.(6,7)

The lack of a rigorous geometrical description of the porous structure of paper has led to the development of theoretical models to describe the porous nature of the sheet. The first model used has been called the simple capillary model. Paper is considered to be a solid material containing a bundle of long thin parallel capillaries. The capillaries are of constant circular cross-section and all have the same radius. Many adaptations to this simple model have been put forward, such as, incorporating a distribution function to control the range of the capillary radius,(8) accounting for changes in dimensions along the length of the capillary,(9) introducing the concept of tortuosity(10) and hydraulic radius.(11) Attempts have been made to put the structure of paper on a theoretical basis. These are based on two-dimensional ideal fibre networks, described in terms of statistical geometry.(12,13) A three-dimensional model is composed of several two-dimensional planes put on top of each other. The result is the multi-planar grid model which enables a prediction to be made of the pore size distribution.(14) The success of these models, however, is somewhat limited, but they have been used to obtain quantitative data for the size and number of pores penetrating a sheet of paper.(15–17)

Where the free surface of a liquid meets a solid, the two intersect at a definite angle, θ, which depends on the nature of the liquid and of the solid. Maximum wetting occurs when $\theta = 0°$, partial wetting when $0° < \theta < 90°$ and no wetting when $\theta \geqslant 90°$. Attempts have been made to explain the phenomenon of wetting and contact angle using the concept of surface energy. However, this approach has been hindered due to the difficulties in measuring surface energies for solids(18,19) which are also influenced by absorption, surface topology and the presence of minor chemical constituents. The contact angle has been found to be dependent on a multitude of factors including moisture content, roughness and heterogeneous composition of the surface, and time.(20–31)

It has been concluded that the macroscopically measured contact angle of a liquid on a surface is a mean of a distribution of local contact angles.(32) Receding contact angles after the surface has been wetted with water have been observed to be always zero.(27, 29) In addition, time must occur between the solid and liquid being brought together to the point where the liquid has wetted the solid. This is generally referred to as a wetting time. For a particular system the wetting time is most influenced by the flow properties of the liquid, since flow must occur in the wetting process. Hoyland(33) and Field(7) showed that the wetting time was dependent upon the roughness of the base sheet and the viscosity of the penetrating solution and reported wetting times in the range 0·005 to 0·3 seconds for unsized sheets. Bristow(34) showed sized papers to have wetting times of the order 0·1 seconds for water and Beazley(35) has reported wetting times for both sized and unsized paper of the order 0·05 to 0·1 seconds.

The application of flow principles to paper is limited to conditions of laminar flow and simple models. Several penetration equations can be derived, the most well-known being the Lucas–Washburn equation(36)

$$l^2 = \frac{r\sigma \cos \theta}{2\eta} t \qquad . \quad . \quad . \quad . \quad . \qquad (1)$$

where l = depth of penetration in time t,
r = pore radius,
σ = surface tension,
θ = contact angle,
η = viscosity.

Penetration equations have been derived to account for the effect of gravity or for any externally applied pressure.(37) The tortuosity factor can be included. A model has been suggested where the pores can be assumed to be long narrow parallel-sided slits in the matrix.(38)

Brecht has stated that the Lucas–Washburn equation adequately describes the penetration of oils and non-swelling liquids into paper.(39) This statement is justified by the findings of many workers.(34, 40–44) Non-swelling liquids include ordinary mineral oils, varnishes, printing inks and many organic liquids used as solvents in various applications. They do not interact with the fibre, do not swell it, nor absorb into it, at least to any great extent. In addition they usually wet the fibre surface easily and have a low vapour pressure. The result is that the only real path for penetration is capillary flow through the pores. Work by Back(45–47) however provided information to show that the pore size may be too strained a concept. Using a capillary rise technique to investigate penetration, he concluded that the fundamental restriction of the Lucas–Washburn equation is the interpretation of the meaning of the pore radius.

The penetration into paper of those liquids which can swell cellulose is complicated by the variety of paths that the penetration may follow. These can be listed as:

1. liquid penetration through the pores by capillary flow
2. liquid movement through the pores by surface diffusion
3. liquid movement through the fibres by various processes
4. vapour phase movement through the pores.

For many years following the formulation of the Lucas–Washburn equation, interest was centred on the applicability of this equation to aqueous penetration and various workers have reported applicability of either part, or all, of the Lucas–Washburn relationship.(34, 48–53) Ranked against this is a lot of information which indicates that Lucas–Washburn equation is inadequate to describe the penetration of water and aqueous solutions into paper.(22, 54–59) Continuous measurement of aqueous penetration has been accomplished by Beazley *et al.*(35, 60) using a reflectance technique. In all cases, with sized and unsized sheets, a very fast initial rate is observed. This is followed by a slower linear penetration. Field(7) and Hoyland(33) have studied the penetration of water and starch solutions of different solids contents into unsized papers with degrees of beating ranging from 25 to 67° SR. Penetration curves similar in shape to those of Beazley were obtained, showing a fast initial rate of penetration followed by a slower rate.

Swelling

IT HAS been known for a long time that fibres take up moisture. The uptake of water is the cause of many property changes. Of major interest in this work are the dimension changes or swelling. Water in a saturated wet fibre has been classified into three types. These are normally referred to as the water of constitution, imbibed water and free water. Water of constitution is that which remains at zero relative vapour pressure. It is held by fairly strong valence bonds, probably hydrogen bonds, has an abnormally high density, does not act as a solvent, does not react to humidity changes and appears to be in a solid state. It is suggested that this water forms a monolayer on the cellulose surface. The amount existing in this state is probably less than 1 per cent bone dry basis.(61) Imbibed water is all that water which is held by the fibre wall, probably forming further layers on top of the basic monolayer. The amount of water in the imbibed state varies, but is usually of the order 30 to 60 per cent bone dry basis and this level is frequently termed the fibre saturation point. Free water is that held by the fibre after fibre saturation. This is held by capillary forces. The amount of free water held by a fibre depends upon the degree of beating and the nature of the lumen, and may be as high as 200 per cent bone dry basis.

For swelling to occur, any system must satisfy the following criteria. Firstly, there must be large units which can separate from each other while remaining definite entities; secondly, there must be localised cohesion between these units, otherwise solution and not swelling will occur directly; and thirdly, a liquid must be used which can release all the other forces which hold the large units together. Cellulose fibres are composed of large molecules held together in ordered and disordered regions, commonly known as the crystalline and amorphous regions, and water forms hydrogen bonds with any strong electronegative group, for example hydroxyl groups. When placed in water cellulose fibres only swell to a limited extent. The limited swelling is due to the penetration of water into the amorphous regions and its failure to penetrate into crystalline regions. The amorphous regions tend to ‘dissolve’, the cellulose molecules moving apart and so giving room for the water to enter, but the cellulose molecules cannot break away completely since they are held firmly in the crystalline regions. As the fibre molecules are pushed apart by the absorbed water molecules, the resulting distortion of the fibre sets up internal stresses which influence the moisture sorption. This effect is analagous to osmotic phenomena and Barkas(62) has applied thermodynamic relationships to swelling similar to those applicable in osmosis.

The swelling process occurs by the local exchange of positions between molecules of the fibre and the molecules of the water. Molecules of the fibre move into and occupy space previously occupied by water molecules and thus the fibre increases its dimensions. Concurrently molecules of water diffuse into the fibre and occupy positions previously occupied by fibre molecules.(63, 64) The whole process of exchange of molecular positions constitutes diffusion. It must therefore be possible to describe the process in terms of the basic diffusion equation, which can be written:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c,}{\partial x^2} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where c = concentration of diffusing matter,
x = distance in the direction of diffusion,
t = time,
D = diffusion coefficient.

The system can thus be characterised by a diffusion coefficient. The value of the diffusion coefficient is however an exceedingly sensitive function of the amount of water already present in the fibre.(64–66) The value of the diffusion coefficient is much lower for the nearly dry than for the more swollen fibre, thus water is absorbed slowly initially, but once absorption has occurred the diffusion becomes faster and a rapid build-up in absorption is observed. The fibres undergo changes in dimension during sorption and swelling in water, and the increases in size are found to be of the order 30 per cent of the original width in the cross-direction and 1 per cent of the original length in the axial direction. The orientation of the main bulk of the molecular chains essentially in a direction parallel to the fibre axis is sufficient to explain this anisotropy.

These measurements are at equilibrium swelling, the degree of swelling increasing as the degree of beating increases. The degree of swelling is also influenced by fibre type, and appears to be roughly proportional to the hemicellulose content of the fibre.

Cellulose also swells to varying extents in a variety of liquids and solutions. Much interest has been centred on the swelling of cellulose in sodium hydroxide solutions. Neale(67, 68) assumed that cellulose behaves as a very weak monobasic acid forming a sodium salt according to the law of mass action. Excess alkali is also taken up, without chemical reaction, in an amount to satisfy the Donnan equation of membrane equilibrium. The resulting unequal distribution of ions causes a movement of water which distends the cellulose until the osmotic pressure is balanced by the forces arising from the cohesion of the cellulose structure. Not all experimental data is explainable in terms of the Donnan equilibrium.(69) Warwicker(70) has postulated that swelling with sodium hydroxide solutions involves, mainly, the moving apart of sheets of cellulose chains, which are held together by Van der Waals' forces. Alkali solution enters the network and pushes the chains apart and loosens the interconnecting secondary bonds. The sheets probably react with caustic soda to form a complex, but these sheets then aggregate with a variable caustic soda and water content between them. He concludes that the swelling of cellulose with caustic soda cannot be taken as typical of all swelling agents.

Dobbins(71) has applied the 'flickering cluster' theory of the structure of water to the swelling of cellulose. Water is regarded as having an extensive hydrogen bonded structure of ice-like clusters which exist in equilibrium with highly reactive unbound monomeric water molecules. Swelling is explained by regarding the monomeric water molecules as the actual swelling agent. The ability of various solutions to swell cellulose depends on the influence of the solute on the equilibrium between the clusters and the monomeric water molecules.

The swelling of a web of paper follows a similar path to the swelling of fibres, but is complicated by the nature of the web. Fibres are treated to different extents, and thus the paper swelling will vary with the degree of beating of the component fibres. Robertson(72) has suggested that the swelling of paper is a function of the release of dried-in stresses and the bond strength between fibres, but recognises that other effects are also involved. The ratio of the degree of swelling in the three directions has been given as 1:2:50 for machine direction: cross-direction: Z-direction.(73) The swelling of machine-made paper is accompanied by the relaxation of some of the dried-in stresses and on subsequent drying the volume of the sheet is usually greater than before. Also the swelling of paper must involve the separation of the fibres, resulting in a loss in sheet strength, due to the breaking of bonds between fibres. Work by Christensen,(82, 83) on the mechanism of sorption and swelling of thin wood sections, has indicated that sorption and swelling is controlled very much by the specimen's kinetic history. The data on the swelling of paper leads to the conclusion that swelling corresponds to the uptake of imbibed water and that the uptake of free water is not accompanied by any swelling.(73)

Very little appears to be recorded about the kinetics of absorption and swelling of cellulose fibres and paper. King and Cassie(74) report that fibre adsorption is virtually instantaneous, the controlling process being the time to diffuse from fibre surface to fibre interior. Bristow(75) has measured thickness swelling against time for sized and unsized papers. Grebe and Hofer(76) have measured the swelling of coated papers in water using a Laser technique, and postulate that the kinetics of swelling are controlled by a diffusion mechanism.

Mechanism of penetration

THE early ideas of the penetration mechanism followed by water were that the major process was by capillary flow. Wilson(77) suggested that perhaps this was not the case, and that diffusional processes might play an important part. Price *et al.*(78) used opacity and transmittance techniques to show that penetration occurred in two stages. They interpreted the fast initial penetration as being capillary flow, and the slower secondary penetration as being penetration into the fibres. A different picture is given by Verhoeff *et al.*(57) who conclude that there are two well-defined paths of penetration; capillary flow through the pores and diffusional flow through the fibres, both occurring simultaneously. With unsized sheets they state that penetration is so fast that it is impossible to separate the two, but with sized sheets they state that the diffusion through the fibres is much quicker than the capillary flow. These conclusions are criticised by Reaville and Hine(79) who say that the primary penetration occurs through the pores. They suggest that the controlling mechanism is surface diffusion ahead of the waterfront, and this is accompanied simultaneously by a secondary penetration into the fibre. A different view is taken by Van den Akker and Wink.(58) They see penetration into a sized sheet occurring in a localised movement, or slip-stick manner, with the localised reduction of the contact angle being the controlling process. This reduction is accompanied by a wave of changing fibre character ahead of, or at, the water/fibre/air interface. The processes involved in this changing fibre character are condensation from the vapour phase, surface diffusion, and penetration into the fibre of sorbed water, presumably accompanied by water movement through the fibre ahead of the interface.

The penetration of water into the fibre is accompanied by swelling. The inter-dependence of swelling and penetration of water into a sheet of paper has been investigated by Bristow.(75, 80) He considers the uptake of water to be the sum of two components, namely: flow into the pores; and penetration into the fibres. The fibre sorption is estimated to a first approximation of the increase in thickness during penetration. He postulated the existence of a boundary parallelogram, on a volume basis. The results from sized and unsized papers could be plotted to show the actual route through the parallelogram. Hoyland(33) and Field(7) concluded that the deviations from the Lucas–Washburn equation which they observed were due to neglect of the swelling of the sheet which occurs as penetration takes place. They put forward a new model for penetration allowing for the water sorption capability of the fibre material and the resultant increase in pore length due to thickness direction swelling. The following penetration equation is derived from this model:

$$l = \left(\frac{\sigma r \cos \theta}{2\eta}\right)^{1/2}(t-t_w)^{1/2}-K\Delta Z, \quad . \quad . \quad . \quad (3)$$

where t_w = surface wetting time,
ΔZ = increase in thickness after time t,
K = a constant.

This penetration equation reduces to the Lucas–Washburn equation when used with non-swelling liquids. They concluded that the penetration process is controlled by the processes involved in reducing the contact angle to zero, these being the various diffusional processes, such as vapour phase diffusion and surface diffusion, which occur ahead of the waterfront, and the penetration of liquid water into the fibre.

Experimental

EXPERIMENTS have been carried out to measure the swelling of paper as the sheet is penetrated by various aqueous liquids. This involves measuring simultaneously the penetration of the liquid and the thickness increase of the sheet of paper. The method used to follow the penetration of water and aqueous liquids into paper has been described previously; only a brief description will be given here.(7, 33) The operating principle is the d.c. conductance change produced by the change paper dry to paper wet. A sheet is prepared with several pairs of electrodes in it, varying in depth in the thickness direction and two strips of silver colloid are painted onto the surface of the sheet. The d.c. conductance change is monitored between particular pairs of electrodes, at a known finite depth within the test sheet, as liquid penetrates into the sheet. The change can then be referred to an exact known position within the sheet. By measuring the time from the moment an aqueous solution contacts the sheet to the moment the conductance change occurs at the known position, a penetration time to that point can be evaluated. Hence a picture of the aqueous penetration can be built up. The following method was employed to measure the thickness increase of the test sheet as the liquid front advanced through the sheet. The test sheet is held in a test rig shown diagrammatically in Fig. 1. The

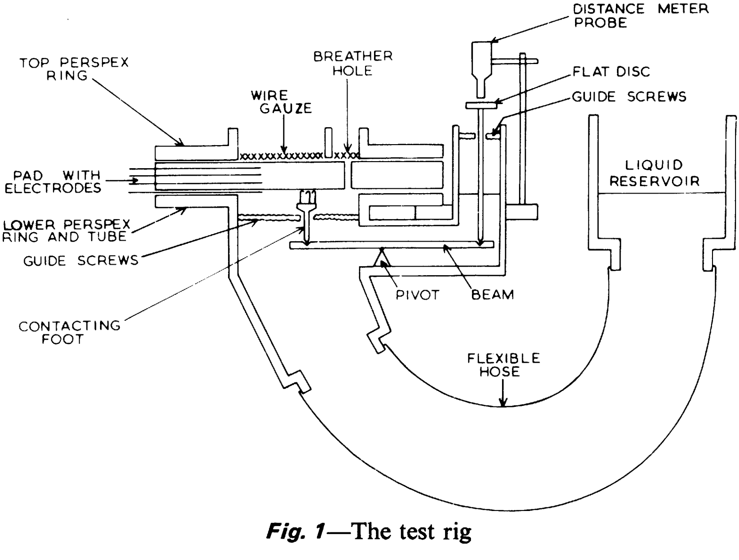

Fig. 1—The test rig

penetrating liquid is contained in a flexible hose connected to a reservoir. The reservoir is lifted mechanically in a controlled manner in order to bring the liquid into contact with the sheet. A beam is pivoted in a side arm attached to the lower Perspex ring and tube. The surface of the sheet is contacted by a foot consisting of three point contacts on the surface of the sheet and a connecting rod, which rests in a notch at the end of the beam. The foot is kept in a vertical position using guide screws. A flat disc is placed on the top of a second connecting rod which rests in another notch at the other end of the beam, again being kept in a vertical position with guide screws. The whole assembly is delicately balanced about the pivot. A distance meter probe is placed above the flat disc. The thickness increases produced as the liquid penetrates the sheet cause the foot to move downwards producing a corresponding decrease in the gap between the flat disc and the distance meter probe. The signal from the distance meter is recorded using the same high speed ultraviolet multichannel recording galvanometer employed to monitor the change in conductance between the electrodes in the sheet. Hence the thickness increase can be correlated directly to the penetration of the liquid.

Results and discussion

THE penetration and swelling of water and aqueous solutions has been studied using the apparatus described above. The same base paper, a bleached softwood sulphate, was used throughout being beaten to 31° SR; no sizing agents or other additives were added. In addition to water, the penetration and swelling behaviour of water containing a wetting agent, a starch solution, cuprammonium hydroxide solution and glycerine containing a small amount of water were examined. The properties of the solutions are listed in Table 1.

TABLE 1—SOLUTION PROPERTIES

	Temperature (°C)	*Ostwald viscosity centipoise*	*Surface tension dynes/cm*	*Density (g/cm³)*	*Concentration*
Water	20	1·00	70·0	1·000	—
Water with wetting agent	20	1·11	27·2	1·001	2·5%
Starch solution	20	3·20	69·3	1·020	5·03% solids
Cuprammonium hydroxide solution	20	1·07	64·6	0·986	3 g Cu/l
Glycerine/water	20	515·0	58·4	1·255	2·9% water

The penetration data obtained from these experiments is shown in Figs. 2, 3 and 4, in the form of depth of penetration *versus* root time plots. The shape of the penetration curves with respect to root time show an initial rapid penetration into the sheet followed by a decrease in the rate of penetration.

Extrapolation of the initial portion of the penetration curves to zero depth

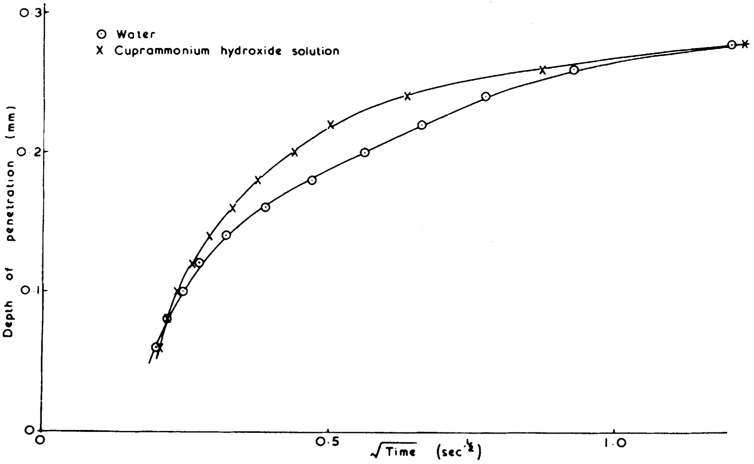

Fig. 2—Penetration curves for water and cuprammonium hydroxide solution

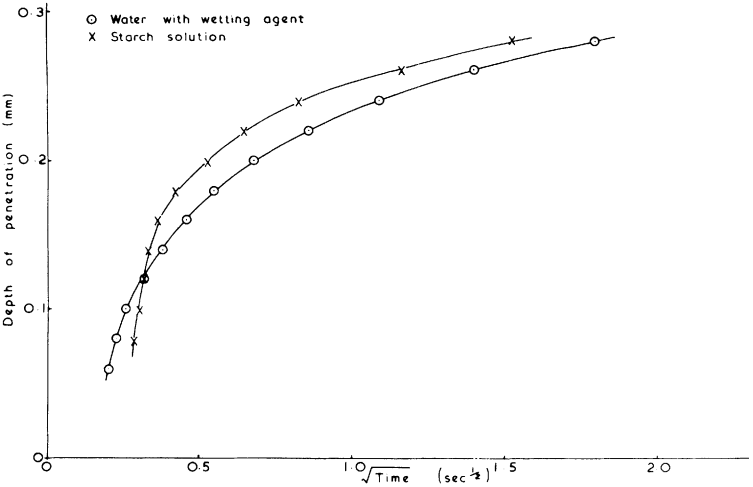

Fig. 3—Penetration curves for water with wetting agent and starch solution

produces a positive intercept on the root time axis. The values of such intercepts squared are the wetting time, t_w, for each penetrant and are shown in Table 2. Penetration, therefore, is not controlled in the simple manner indicated by the Lucas–Washburn equation.

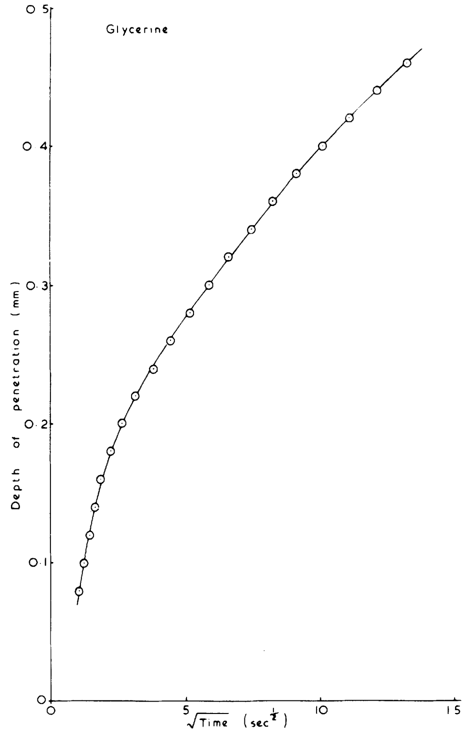

Fig. 4—Penetration curve for glycerine/water

TABLE 2—WETTING TIMES

Penetrant	*Wetting time, t_w (sec)*
Water	0·021
Water with wetting agent	0·017
Starch solution	0·054
Cuprammonium hydroxide solution	0·028
Glycerine/water	0·09

Swelling curves were also obtained simultaneously with the penetration measurements. The increase in thickness of the sheet, ΔZ, is plotted against time for the various solutions in Figs. 5, 6 and 7. The base paper was also immersed in the various solutions for at least 50 minutes and the maximum thickness increase, ΔZ maximum, was measured independently using a micrometer; the results are recorded in Table 3. A comparison of Figs. 5, 6

TABLE 3—MAXIMUM THICKNESS INCREASE, ΔZ max

Penetrant	*Maximum thickness increase, ΔZ max (mm)*
Water	0·147
Water with wetting agent	0·140
Starch solution	0·131
Cuprammonium hydroxide solution	0·183
Glycerine/water	0·049

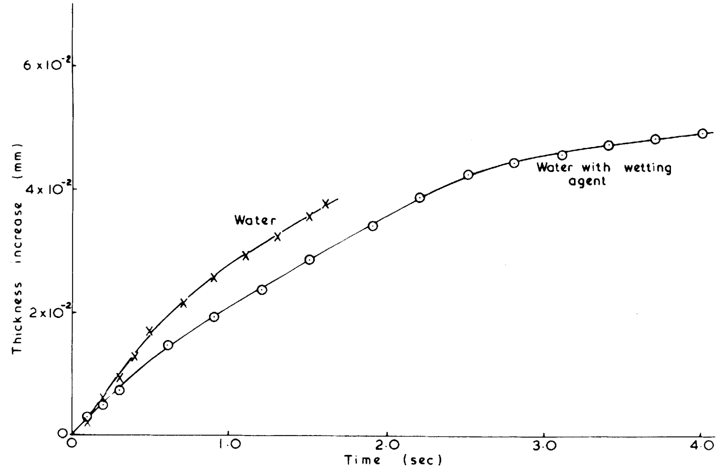

Fig. 5—Swelling curves for water and water with wetting agent

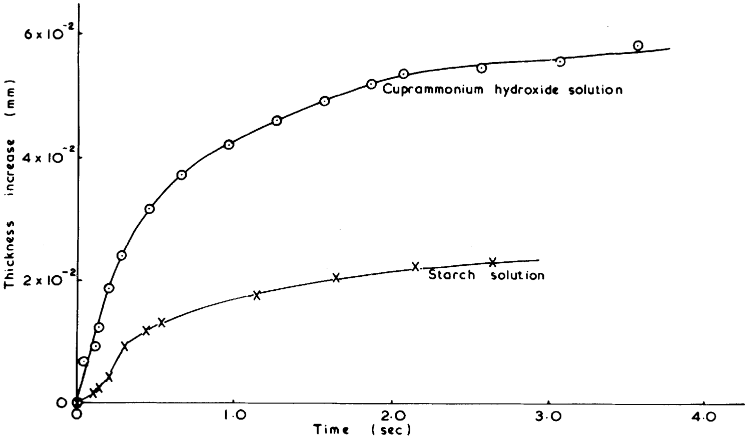

Fig. 6—Swelling curves for starch solution and cuprammonium hydroxide solution

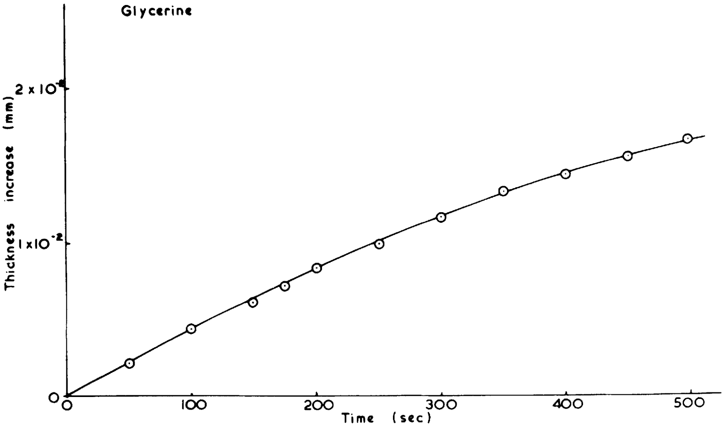

Fig. 7—Swelling curve for glycerine/water

and 7 and the values for the maximum increase in thickness indicate that some 30 per cent of the final swollen thickness of the sheet is attained during penetration of the sheet by the liquid, that is, in the first few seconds after the sheet has been wetted.

The dependence of swelling on penetration can be simply demonstrated by plotting the depth of penetration against thickness increase as shown in Fig. 8. All the aqueous solutions exhibit similar characteristics. During the initial rapid penetration little swelling takes place. However, as the penetration rate decreases so large increases in the sheet thickness are observed. The point at which the thickness increases become significant correspond to the decrease in penetration rate shown in Figs. 2, 3 and 4.

The literature survey has indicated that swelling is a diffusion process and therefore capable of description in terms of the basic diffusion equation commonly known as Fick's second law of diffusion, equation (*2*) above. It is possible to derive from equation (*2*) an expression for the fractional change in concentration in a semi-infinite medium at any point as a function of time.(81) For this derivation it is assumed that at the plane surface of this medium, i.e. at $x = 0$, $C = C_\infty$ at time $t > 0$, and furthermore that at time $t = 0$, $C = C_0$ at $x > 0$. The expression obtained is

$$\frac{C_t - C_0}{C_\infty - C_0} = 1 - \operatorname{erf}\left[\frac{x}{2(Dt)}\right]^{1/2} . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

where C_0, C_t and C_∞ are the concentrations of penetrant at a point x in the sheet at times 0, t and ∞. The total amount, m_t, of diffusing substance taken up through surface area A of sheet in time t can be found by differentiation

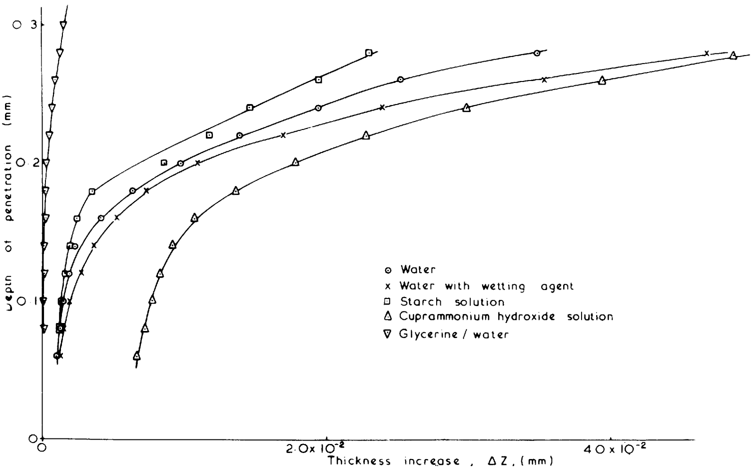

Fig. 8—Depth of penetration *versus* thickness increase

with respect to x of equation (*4*) and then integration of the resultant expression with respect to t to yield

$$m_t - m_0 = 2A(C_\infty - C_0)\left(\frac{Dt}{\pi}\right)^{1/2}. \qquad (5)$$

As the amount of penetrant absorbed after infinite time, m_∞, in a sheet of surface area A and thickness L can be expressed by

$$m_\infty - m_0 = AL(C_\infty - C_0), \qquad (6)$$

it follows that

$$F = \frac{m_t - m_0}{m_\infty - m_0} = \frac{2}{L}\left(\frac{Dt}{\pi}\right)^{1/2}, \qquad (7)$$

where F = fraction of the amount of penetrant taken up in time t relative to the amount taken up at infinite time,

and m = amount of penetrant present at time 0, t and ∞.

A plot of F against root time is thus sufficient for the calculation of D with equation (7) from the slope of the graph obtained. F can be estimated from $\Delta Z/\Delta Z$ max where ΔZ is the thickness increase after time t and ΔZ max is the maximum thickness increase. A typical example of $\Delta Z/\Delta Z$ max *versus* root time is shown in Fig. 9. The graph is initially nonlinear indicating that the diffusion coefficient at the commencement of swelling is not constant but increases to a maximum value. The gradient of the graph was measured between specific time intervals and an apparent value of the diffusion coefficient was calculated using equation (7). The results of this calculation

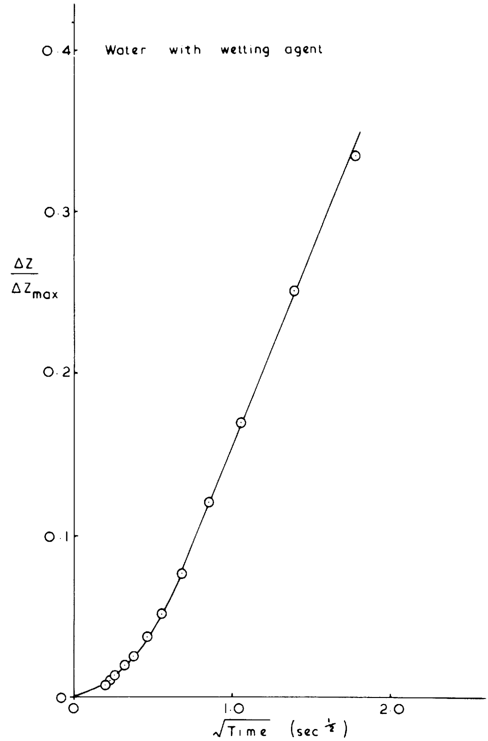

Fig. 9—Fraction of thickness increase relative to maximum thickness *versus* root time

are shown in Figs. 10 and 11. It can be seen that for each aqueous solution the apparent diffusion coefficient increases to a maximum value as penetration proceeds through the sheet. The diffusion coefficient must be referred to as an apparent diffusion coefficient because it is realised that the above analysis is by no means rigorous and the values calculated for the diffusion coefficient cannot be regarded as absolute values. Nevertheless the calculated values are of the same order of magnitude as those calculated for textile fibres.(65)

The model for penetration proposed by Hoyland and Field can now be evaluated using the apparent diffusion coefficients. Rearranging equation (*3*) gives

$$K\Delta Z = \left[\left(\frac{r\sigma\cos\theta}{2\eta}\right)^{1/2}(t-t_w)^{1/2}-l\right]. \qquad (8)$$

Due to the difficulties which have been encountered in defining the concept

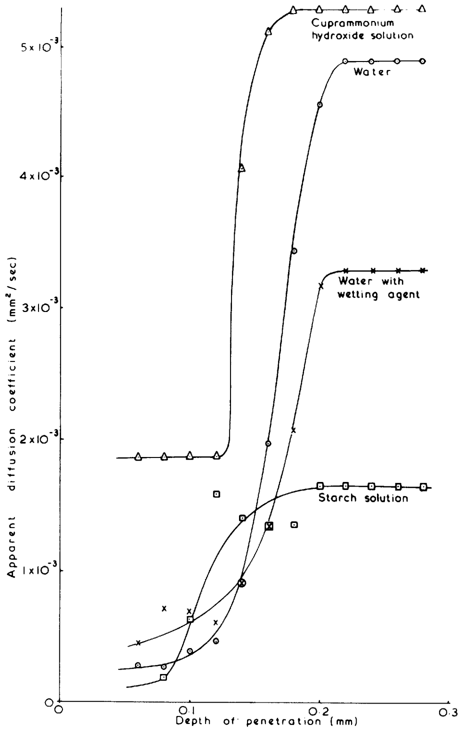

Fig. 10—Apparent diffusion coefficient against depth of penetration

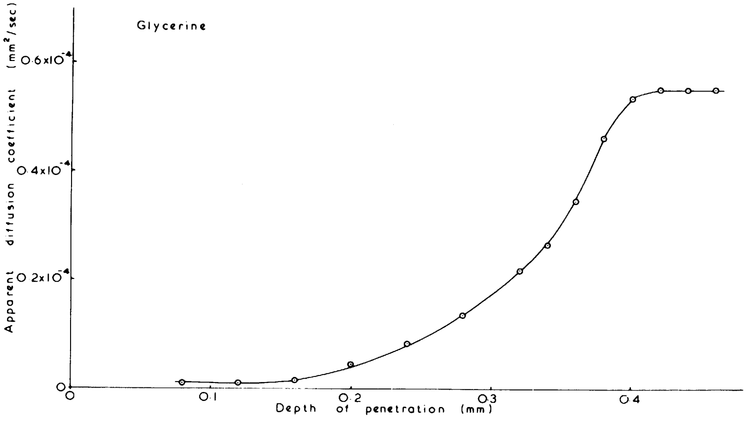

Fig. 11—Apparent diffusion coefficient against depth of penetration

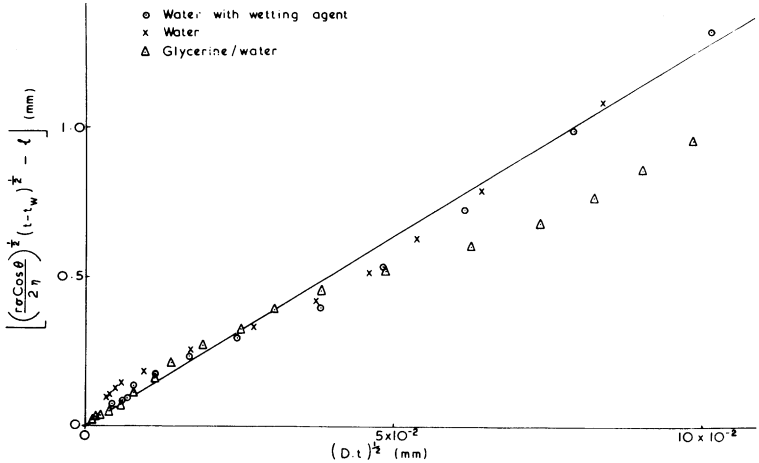

Fig. 12—$\left[\left(\frac{r\sigma\cos\theta}{2\eta}\right)^{1/2}(t-t_w)^{1/2}-l\right]$ against $(Dt)^{1/2}$ (mm)

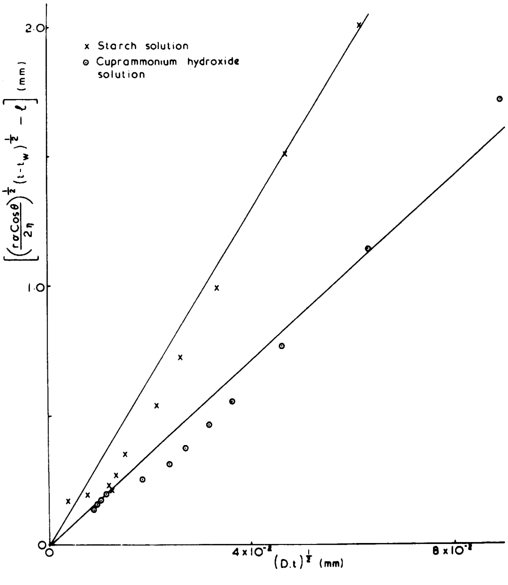

Fig. 13—$\left[\left(\frac{r\sigma\cos\theta}{2\eta}\right)^{1/2}(t-t_w)^{1/2}-l\right]$ against $(Dt)^{1/2}$ (mm)

of pore radius and even its measurement, and also due to the difficulty in measuring contact angles for unsized papers, the initial slope of the depth of penetration *versus* root time curves was measured and taken as a measure of $(r\sigma \cos \theta/2\eta)^{1/2}$ for each penetrating solution. The wetting time t_w and the depth of penetration l are also known. The above theory states that the increase in thickness ΔZ is proportional to $(Dt)^{1/2}$ where D is the apparent diffusion coefficient. A plot of

$$\left[\left(\frac{r\sigma \cos \theta}{2\eta}\right)^{1/2}(t-t_w)^{1/2}-l\right] \text{ versus } (Dt)^{1/2}$$

should therefore give a straight line. Such plots are shown in Figs. 12 and 13. A reasonable degree of linearity is observed in all cases, showing that deviations from the Lucas–Washburn equation for aqueous penetration are due to the neglect of the swelling of the sheet in the penetration equation and that the thickness increases observed during penetration are controlled by a diffusion mechanism.

Conclusions

It has been shown that the swelling of unsized sheets of paper is an integral part of the transudation of aqueous liquids into paper. The thickness of the web increased to 30 per cent of its final swollen thickness as the liquid penetrated into the sheet from one surface to the other. The swelling accounts for the deviations from the Lucas–Washburn equation which are observed during the penetration of aqueous liquids. The thickness increase of the sheet appears to be controlled by a diffusion mechanism and apparent diffusion coefficients can be calculated from the swelling data using a simple model. Further work is obviously necessary to quantify the diffusion model, but it is suggested that the moisture content is probably the most significant factor controlling the diffusion process.

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Discussion

Mr J. B. Sisson I hope that in your future work you will consider the great variety of density in paper structures that exist. In glassine for example you might get a density similar to that of cellulose whereas in some of the tissue products you may be approaching a density of about 0·1 and in the latter case rather than finding the structure swells in fact you will find it collapses because of the flexibility of the fibres.

Hoyland I will bear that in mind.

Mr J. F. Waterhouse What was the moisture content of your fibres in these experiments?

Hoyland All experiments were carried out under controlled conditions of 50 per cent RH and 20° C; the moisture content of the paper was approximately 8 per cent.

Waterhouse You remember from my presentation that I stated we had achieved some pretty good straight lines of latex penetration into wet webs having a moisture content around the fibre saturation point. I now have a better understanding of these results having now heard your paper.

Dr A. H. Nissan In your figures 12 and 13 you are effectively plotting $t^{1/2}-l$ against $t^{1/2}$. That is rather dangerous because if l is not dominant you will always get a straight line. Can you satisfy my doubts?

Hoyland Yes, l is dominant. Also, we are plotting against the square root of the product of the apparent diffusion coefficient and time. The apparent diffusion coefficient is not a constant but increases as penetration proceeds.

Dr J. M. Haynes Would you enlarge upon the physical significance of the

Under the chairmanship of Prof. M. Judt surface wetting time, t_w? Does the swelling process exhibit a similar induction period?

Hoyland Presumably the surface wetting time is the time before one achieves a monolayer coverage of the surface thereby reducing the contact angle so that the liquid can then enter the body of the paper. Initially we did suspect that there may be a period of time before swelling commenced, but we came to the conclusion that this would be so small that we could neglect it.