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FUNDAMENTAL PARAMETERS RELATING TO PERFORMANCE OF PAPER AS A BASE FOR AQUEOUS COATINGS

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Synopsis In relating the quality of the coated sheet to the properties of the base paper, the liquid absorbency of the base paper is a most important consideration for all coating processes.

Nor surprisingly, base sheet absorbency has received a great deal of published attention. Recently, there has been a growing appreciation that the Lucas-Washburn equation does not fully explain the penetration of aqueous fluids into paper. The shortcomings of the Lucas-Washburn equation are clearly indicated in the work described on the mechanism of the size press.

A new method of following the penetration of aqueous solutions and suspensions is presented.

Analysis of the results indicates that a wetting time exists and that the Lucas-Washburn equation is inadequate to describe the penetration of aqueous fluids into paper.

A new model for penetration is suggested, which allows for the swelling of the sheet that occurs as penetration takes place. A penetration equation is derived from this model.

Introduction

THE pigment coating of paper is governed by four main variables—

1. The specification for the finished paper
2. The coating fluid and its formulation
3. The coating machine
4. The coating base paper.

All of these main variables may be broken down into components and, furthermore, they interact with one another. Thus, it is quite impossible to discuss one of them without reference to the others. This paper is concerned

Under the chairmanship of Prof. M. F. Judt with the relevant properties of the base paper and the effect of variations in these properties on the quality of the coated paper; but, to discuss this subject sensibly, we must consider the other main variables and their interaction with the coating base.

Specification for the coated paper

THE whole point of pigment coating paper is to produce a satisfactory sheet for publishing. The term publishing includes printing and the associated paper property levels required in the various printing processes. It also includes properties that determine the appearance and utility of the printed sheet such as gloss and stiffness. These properties determine the formulation of the coating mix. To give but two examples, the whiteness specification determines the pigment used; the pick specification determines the binder level.

The coating mix

THE simplest coating mix consists of a suspension of pigment particles in an aqueous solution of adhesive, for example, clay in starch.

This simple system is rarely, if ever, found in practice. There may be added to it an emulsion of latex, often a dispersion in water at about 50 per cent solids. The water from this addition dilutes the starch solution and we are left with a suspension of clay and latex in a starch solution. It is important to remember that the liquid component of this system is starch solution, with the appropriate viscosity. Similar considerations apply *mutatis mutandis* to casein systems, should there be any still to be found. Alternatively, there has been a growth, comparatively recently, of the use of coating mixes whose binder is entirely latex emulsion. In these systems, there is a suspension of latex and clay (or other pigment) in water. The liquid component is then water, having lower viscosity (by possibly a factor of 100) and higher surface tension (possibly by a factor of 2) than starch or casein solution. The total solids content of the mix is adjusted of course to give a viscosity suitable for the coating machine in use.

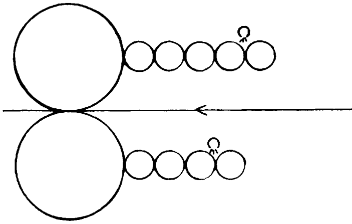
Additives to these basic mixes, although often small in quantity in proportion to other components, may have considerable effect on the rheological properties of the mix. The most spectacular example is of course the effect of a pinch of dispersant.

The coating machine

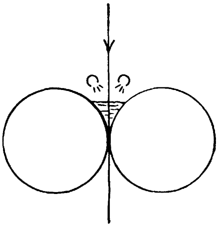
THE coating machine performs four functions—

1. Application of wet coating mix to the paper
2. Metering to some predetermined quantity
3. Smoothing the wet mix on the paper
4. Drying by evaporation of the water from the mix.

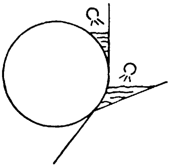
The four functions are not necessarily carried out separately, as is seen by reference to Fig. 1–3, which illustrate the basic types of coating machinery. In all the roll coaters, the application and metering functions are performed



(a) MASSEY



(b) SIZE PRESS



(c) BIL BLADE

Fig. 1—Roll coaters

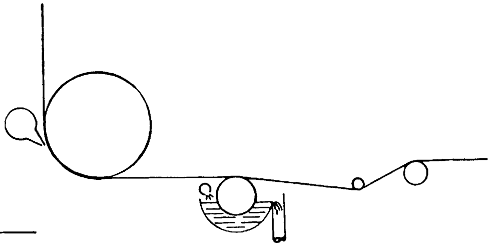
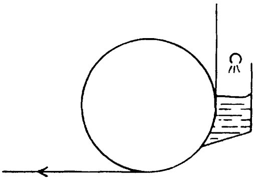
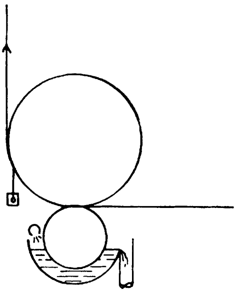


Fig. 2—Airknife coater



(a) PUDDLE



(b) FLOODED NIP

Fig. 3—Blade coaters

simultaneously in the nip and no subsequent smoothing of wet coating is carried out. In (*a*) and (*b*), the wet coating emerges on the paper as the result of a film split at the outgoing side of the nip. The Bilblade (*c*) is a hybrid in which the film split applies on one side and the smoothing action of the blade on the other. These three coaters are most often encountered as part of the papermachine itself—in other words, they are on-machine coaters. In the airknife coater, application of coating mix to paper is performed by the lick-up roll and metering and, possibly, some smoothing by the air knife. In the first of the two systems of blade coating (often called the puddle type), application, metering and smoothing are inextricably mixed. In the second (the flooded nip), application is separated from metering and smoothing. In all coaters where application is by roll, some metering may be introduced by the fitment of a gate roll. In all the systems considered, drying is a quite separate function taking place after all the others. Even though the drying system can have a significant effect on the coating properties, its consideration is not within the scope of this paper.

It is suggested that the important features of coating processes that interact with the base paper variable are—

1. Whether or not the paper is compressed and subsequently allowed to relax in contact with wet mix.
2. Whether there is any significant time interval between the application of wet coating and a subsequent smoothing operation.

In the analysis of coating processes, more has been published on blade coating than on any of the others. The classic work of Follette & Fowells$^{(1)}$ indicated the characteristic dependence of coating weight applied on speed of running. This relationship is in the form of a curve (Fig. 4) with a minimum value of coating weight, generally at a comparatively low speed for blade coating. Subsequent analyses, Windle & Beazley,$^{(2, 3)}$ Bohmer,$^{(4)}$ Turai$^{(5)}$

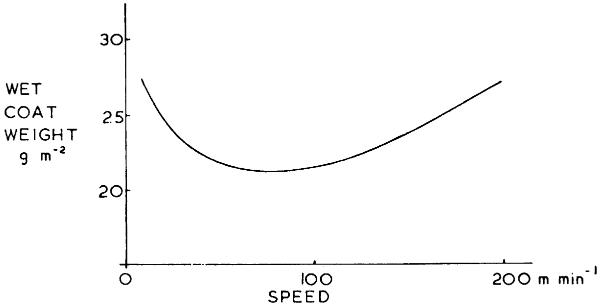


Fig. 4—Typical blade coater coat weight/speed curve

and Bleisner(6) have, in the main, concentrated on the rising part of the curve, at speeds higher than the minimum pick up. This is not unreasonable in the sense that these speeds are more relevant to the general run of blade coating. The mathematical work has been concentrated on the development of the hydrodynamic force normal to the blade, acting in opposition to the imposed, blade pressure. These forces tend to increase coating weight as speed and viscosity are increased. The results of these calculations give a term in the coating equation of the form $K(\eta S)^y$ where η and S are mix viscosity and speed, respectively, K is a quantity dependent on the assumptions made about the geometry of the blade and boundary limits and y is a power, often about 0·5. Windle & Beazley(3) have introduced further considerations involving the viscoelastic forces generated by shearing high solids mixes. Bohmer(4) has given rather more consideration to the entire shape of the speed/pick-up curve. He reports two important effects: as the sheet roughness is increased, the curve moves bodily upwards and as the mix viscosity is increased, the speed of minimum pick-up is reduced.

This characteristic relationship between speed and pick-up has been found to apply in the size press treatment of paper.(7, 8) From this work, an equation has been proposed to represent the pick-up over the whole range of speed. The equation is—

$$P_u = K_1 + \frac{K_2}{(\eta S)^n} + K_3(\eta S)$$

where P_u is the pick-up, η the viscosity of the solution, S the speed of the sheet through the size press, n is a number and K_1, K_2 and K_3 are coefficients. In this equation, the pick-up is the sum of three terms—respectively, the immobilisation term, the absorption term and the hydrodynamic term. A similar breakdown is given qualitatively by Bohmer(4) for blade coating.

The airknife coater has received very little attention from the publishers. McFarlane & Hoath(9) at the last symposium gave an analysis of the process leading to the design of a coating weight control system. No account is taken of the effects of base sheet properties in this paper, except in so far as migration of binder into the sheet necessitates the addition of water to mix returned on recirculation.

Coating base paper

FROM the foregoing considerations, it appears that the base sheet properties relevant to the coating operation are roughness and absorbency. Roughness affects the weight of coating picked up and retained through the coating process. In the airknife process, it also affects the roughness of the finished coated sheet.(10)

Absorbency affects the coating operation in a quite fundamental way. Binder lost into the sheet is not available to bind the coating. Thus, a high degree of absorbency in the sheet results in a higher level of binder being required in the mix formulation to match the pick specification on the finished sheet.(11)

Comparison has been made between the behaviour of the size press and the blade coater. In the importance of base sheet absorbency, there is one important difference between the two processes. In the size press, absorption of solution by the sheet has no effect on the remaining solution in the pond. For blade coating, however, absorption of binder increases the solids content of the wet mix remaining on the paper. With blade coaters running high solids mixes, this may have a profound effect on the performance of the blade, particularly in the flooded nip arrangement.

With these considerations in mind, the remainder of this paper will be a report of experimental work carried out at UMIST in an attempt to evaluate the mechanism of absorption of aqueous fluids by paper.

Absorption term in size press equation

IN THE course of our size press investigation, a great many curves of pick-up against speed were obtained.(34) These covered a range of solution viscosity, roll hardness and degree of beating in the base sheet. The rising part of these curves (for example, CD in Fig. 5) is a straight line for those uses in which both rolls are hard (that is, steel). This is in accordance with hydrodynamic theory.(8) These 'hard roll' curves were analysed in the following way.

The basic, working assumption equation is—

$$P_u = K_1+\frac{K_2}{(\eta S)^n}+K_3(\eta S) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $K_3\ \eta$ is the slope of the straight, rising branch of the curve and may be measured from the curve. Calling this slope M—

$$P_u-MS = P_u' = K_1+\frac{K_2}{(\eta S)^n} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The value of P_u' asymptotically approaches K_1, which is thus determined.

Having thus found M and K_1, we may compute $P_u'' = P_u-MS-K_1$ for values of S.

Then, $P_u'' = K_2/(\eta S)^n$ and $\ln P_u'' = \ln K_2\, n\, \ln(\eta S)$ . . . . . (3)

A plot of $\ln Pu''$ against $\ln S$ then gives K_2 and n. Employing this analysis, it was found that—

1. The coefficient K_1 depends on the degree of beating in the sheet and is independent of solution viscosity and machine speed.
2. The coefficient K_3 is independent of sheet properties and its value may be calculated by hydrodynamic principles as indicated by Hoyland & Howarth.(8)
3. The coefficient K_2 and n are both dependent on the concentration of the sizing solution. In our work, this was related only to viscosity, though we would expect K_2 to depend on surface tension, which also varies with concentration. The value of K_2 depends of course on the sheet. In our case, this was related to degree of beating, since no internal sizing was applied to the papers we used in this investigation.

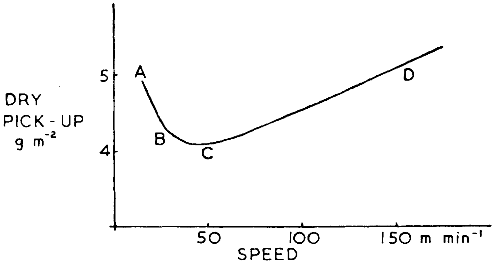


Fig. 5—Size press pick-up/speed curve

It is clear from this work that the level of pick-up is set by the value of K_1, a wholly sheet-dependent term and modified by the absorption and hydrodynamic terms, which—at our running speeds (up to 150 m/min)—act as relatively small, correcting terms. At higher speeds, the hydrodynamic term exerts a progressively increasing influence and its behaviour, for the size press, seems to be calculable. The empirical approach to the absorption term is unsatisfactory and necessitated by our lack of basic understanding of the mechanism governing penetration of aqueous fluids into paper.

Absorption of liquids by paper

THE heterogeneous nature of a paper substrate prevents accurate application of the known laws for penetration, permeation and flow that apply to more easily defined systems. Not only do we need to know the number of pores in a paper web, but also their size distribution and direction; assumptions such as circular cross-section are found to be incomplete. Another complication arises with water and aqueous solutions; water and water vapour cause fibre swelling, the exact nature of this swelling and the effect on penetration being uncertain at present. A precise theoretical treatment of penetration is thus impossible, but many attempts have been made from which several conclusions can be drawn.

Nissan(12) has reviewed the possible mechanisms by which fluid can enter a sheet of paper—

1. Vapour penetration through the pores
2. Liquid penetration through the pores by capillary action
3. Liquid penetration through the pores by surface diffusion
4. Liquid penetration through the fibres.

Liquid penetration through the pores by capillary action is generally considered to be the dominant mechanism, although the existence of the other three mechanisms must not be neglected. Assuming that penetration proceeds in the absence of externally applied pressure, application of the Hagen-Poiseuille law for laminar flow to a capillary yields the well-known Lucas-Washburn equation.(13)

$$l^2 = r\sigma \cos\theta \, t \, / \, 2\eta$$

where l = thickness of the penetrated layer
r = radius of the capillary
σ = surface tension
θ = contact angle between the liquid and boundary wall
η = viscosity of the liquid
t = time.

When dealing with the pores in a sheet of paper, we do not have long thin capillaries. The pores in paper are usually very short in relation to their diameters, they are not all the same size, frequently interconnect and are not cylindrical. Correction factors have been applied to the Lucas-Washburn equation. Tollenaar(14) introduced a Gaussian distribution of the pore radii. Kozeny(15) put forward the concept of hydraulic radius (that is, the ratio of the volume of the pores to their surface area) and modification of Kozeny's theory by Carman(15) led to the Kozeny-Carman equation relating hydraulic radius to permeability data. Corte's(16) work on the structure of paper shows agreement with the Kozeny-Carman equation under conditions of laminar flow.

Nevertheless, the Lucas-Washburn equation has had considerable success in describing the penetration of non-swelling liquids such as oils(17) and printing inks(18) into a sheet of paper.

Deviations from Lucas-Washburn have been found for the penetration of swelling liquids and in particular aqueous solutions. Van den Akker(19) using a fluorescence size test found that his results are best explained by assuming that the depth of penetration is proportional to time raised to the power 1, not 0·5 as predicted by the Lucas-Washburn equation.

The concept of a constant value for contact angle is almost certainly unrealistic and has been criticised.(19, 20) For sized papers, it is generally agreed that the rate of penetration is controlled by the time required in bringing the contact angle down below 90°.

Bristow(21, 22) and Van den Akker(19) found that the amount of liquid taken up by a sheet of paper was dependent on two factors—an amount depending on the roughness of the sheet and that due to capillary penetration. Later work by Bristow(23) shows that swelling cannot be neglected. He indicates that for an unsized paper liquid is taken up simultaneously through the pores and through the fibres; with a sized paper, liquid penetration is initially through the fibres, then via the pores when the effectiveness of the sizing agents present has been overcome.

The migration of coating colours into paper has been studied by Windle & Beazley,(24, 25) who came to the conclusion that migration is an integral part of the whole coating process. All the penetration versus root time curves they presented showed an apparent intercept along the time axis, indicating that wetting must take place before penetration can start.(25) For unsized papers, they found that liquid entered the sheet at a constant rate. With sized papers, however, there was an initial very rapid penetration followed by a slower rate of penetration. The addition of a wetting agent destroyed this phenomenon. They postulated the concept of defect zones in a sheet when penetration of liquid occurred very quickly, probably by surface diffusion and this was then followed by a slower bulk penetration through the pores.

Hence, it appears that no exact explanation can be given to account for the penetration of aqueous liquids or suspensions into a sheet of paper. We can conclude that this penetration depends on the state and nature of the paper surface and on some function relating the properties of the penetrating liquid with the porous structure of the base sheet. It was therefore decided to measure the penetration of aqueous liquids into paper in order to try and establish the latter relationship.

Experimental

MANY methods have been used to measure the penetration of liquids into paper. The Warren test(26, 27) is used to measure the water retention of coating colours and measures the change in electrical conductivity of the sheet as penetration takes place. The presence of a single pinhole, however, allows current to flow and it is found that it is impossible to relate depth of penetration to changes in conductivity.

Many sizing tests have been employed. Two recent examples are the fluorescence dye technique of Van den Akker(19) and the use of Cobb test by Bristow.(22, 23, 28) The technique of using a roller and inclined plane(35) and a similar apparatus that doctors a known amount of liquid on to the surface of a moving sheet(29, 30, 21) is also well known. The above methods, however, do not give continuous measurements of penetration and rely heavily on mathematical analysis of the results, often employing the Lucas-Washburn equation.

Ultrasonic techniques have been tried,(31, 32) in which the change of sonic pulse propagation time between two points is continuously monitored as penetration takes place, but the method does not easily measure the depth of penetration.

The most employed method of measuring penetration continuously uses the principle that the reflectance of paper is reduced when it becomes wet. Optical methods, based on this principle, have been applied to the penetration of inks and varnishes,(18) liquids(33) and coating colours,(24) the depth of penetration being related to optical changes by using Kubelka-Munk theory.

Method used

A METHOD has been devised of directly timing the passage of the liquid front as it advances through a sheet of paper. It depends on the very rapid reduction in the electrical resistance of paper with its absorption of water. Pairs of electrodes are placed in a sheet of paper at the making stage on a sheetformer at several positions through the total thickness. A low voltage (9 V) is applied independently to each pair of electrodes and, when the sheet is dry, it results in an undetectable current in each circuit. When water is applied to one side of the sheet, the advancing water front successively 'shorts out' the pairs of electrodes to cause a rapid rise of current in each circuit, respectively. Feeding the current from each circuit for a pair of probes to a separate channel of a multi-channel recorder produces a trace as shown in Fig. 6. The time at which a given trace indicates the start of the current rise is taken as the time at which the water front reached the relevant pair of probes. It should be emphasised that value of the current or resistance

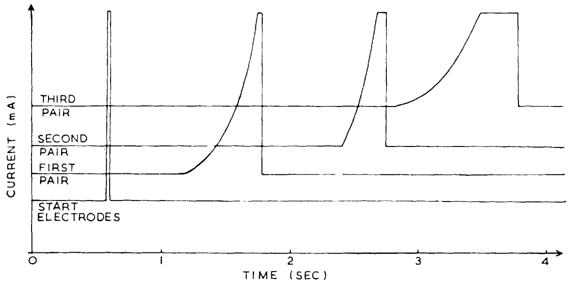
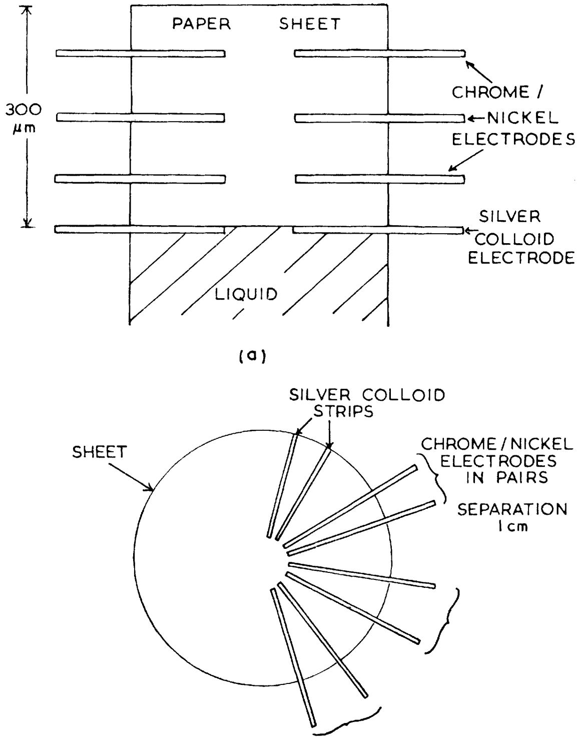


***Fig.* 6**—Typical current trace for water between the probes is not used, hence the uncertain definition of end points in, for example, the Warren tester is avoided.

The distribution of electrodes in the sheet is shown in Fig. 7.



(a)

(b)

Fig. 7—Distribution of electrodes

Preparation of base paper

Preparation of the base paper was subsequently found to be critical in order to obtain consistent results. The following technique is used in preparing sheets and inserting the electrodes. The pulp used is a bleached softwood sulphate and a chrome-nickel alloy ribbon wire of dimensions 0·002 in × 0·020 in is used for the electrodes. A 40 g/m sheet is formed using a British standard sheetmachine and couched off the wire. A second sheet is formed, a pair of electrodes are placed in position, the first sheet is then laid on top; the whole pad thus formed is couched. Repeating this procedure enables a multi-layer pad to be built up with electrodes in position between each layer. The pad is then pressed, dried and conditioned at 50 per cent rh and 20° C. In practice, the electrodes are arranged in pairs around a central point, as shown in Fig. 7. Two strips of silver colloid are painted on to the surface of the sheet and allowed to dry, so that the time when the surface is wetted by the penetrating liquid can be established.

The electric circuit

THE electrical circuit used to follow penetration is shown diagramatically in Fig. 8. Small dc voltages are used and a high speed ultra-violet multi-channel recording galvanometer is employed to record current with time. Each electrode pair is connected to an independent circuit. A hold-in relay system is used to isolate each circuit after the advancing liquid front has reached each pair of electrodes. This is found to be necessary, since inter-circuit interference causes fluctuations in neighbouring galvanometers. The passage of the liquid front through the pad can thus be followed.

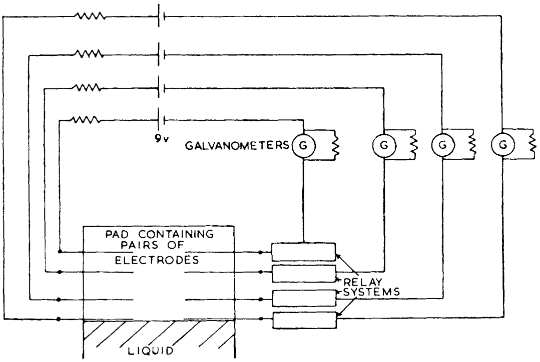


Fig. 8—The electrical circuit

The pad is held in a test rig shown diagramatically in Fig. 9. The pad is clamped between two clear plastic rings. The upper ring incorporates a wire gauze to ensure that the paid is always held in a horizontal position. The penetrating liquid is contained in a flexible hose and connected to a reservoir. The reservoir is lifted mechanically in order to bring the liquid surface into contact with the pad. It was found necessary to put a breather hole in the pad to enable air trapped between the sheet and the rising liquid to escape.

Measurement of position of electrodes

THE depth of each electrode from the surface of the sheet was measured using the method illustrated in Fig. 10. A silver colloid electrode is painted on the surface of the sheet above the chrome-nickel electrode to be measured. The needle is lowered until electrical contact is made with the silver colloid electrode. The switch is changed to isolate the silver colloid electrode and to connect the chrome-nickel electrode into the circuit. The needle is lowered until contact is again established. Readings are taken on the micrometer screw gauge and the depth of each electrode from the surface is thus determined.

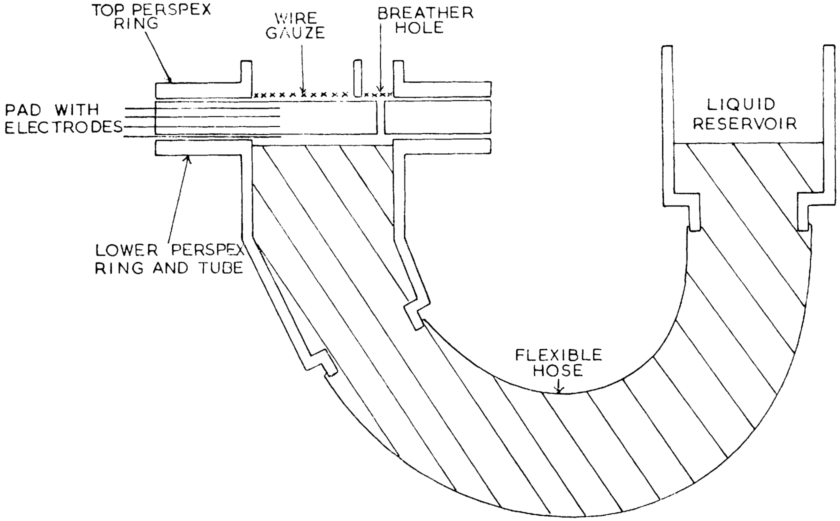


Fig. 9—The test rig

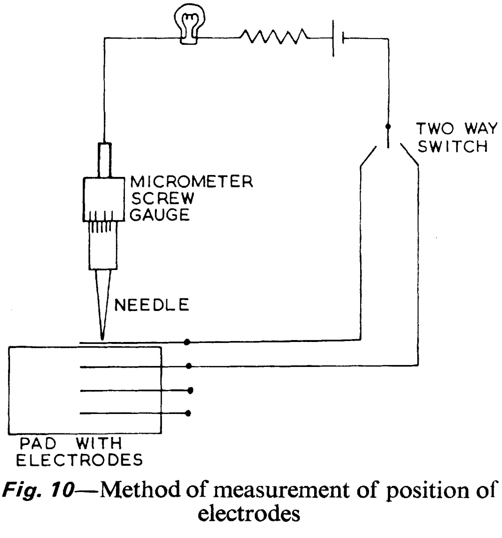


Fig. 10—Method of measurement of position of electrodes

Results and discussion

The penetration of water and starch solution of different solids contents have been studied for papers with degrees of beating ranging 25–67° SR. No sizing agents or other additives were added to the base paper. From these experiments, a depth of penetration versus time curve is obtained. Fig. 11 shows a typical example for the water penetration of a 25° SR base paper. From these curves, the penetration depth versus root time curves can be plotted. Fig. 12 shows the root time plot for water for various degrees of beating of the base paper and indicates how the time of penetration is increased when using a more highly beaten base paper. The root time plots for

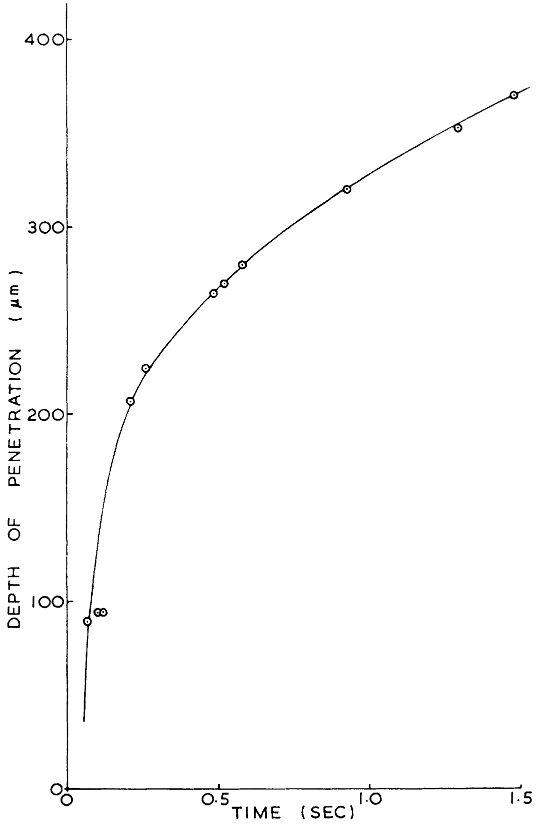


Fig. 11—Depth of penetration against time curve for water, 25° SR base paper

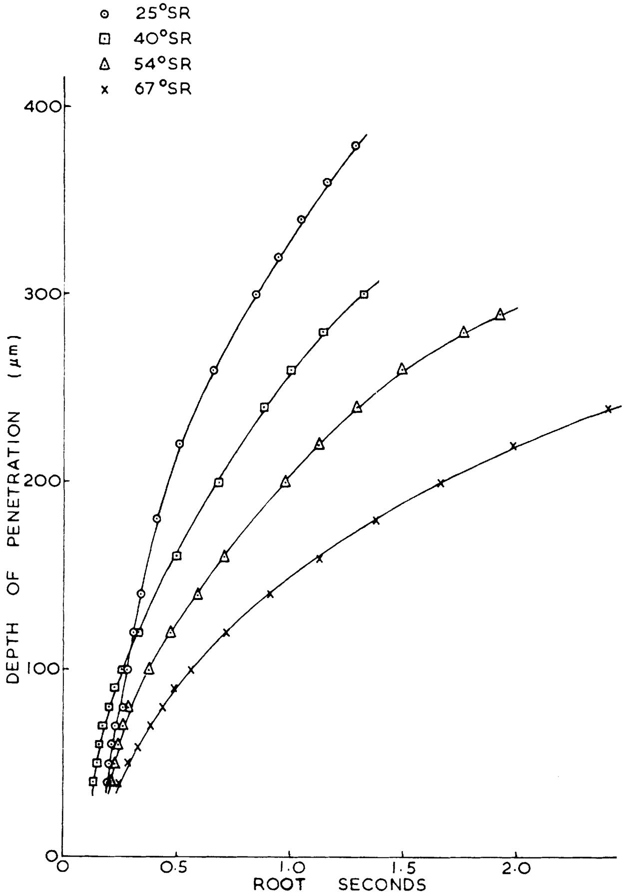


Fig. 12—Penetration curves for water

various starch solutions with a base paper of 54° SR are shown in Fig. 13. All the curves in both sets of root time plots exhibit similar characteristics—namely, an initial, fairly rapid penetration into the sheet, followed by a much slower rate of penetration. Secondly, if the initial portion of the curves is extrapolated to zero depth, the line cuts the root time axis with a positive intercept and an apparent wetting time can be measured. (The term apparent wetting time is used, because the extrapolation to zero assumes a linear relationship between depth of penetration and root time over the first part of the curve; this may not be so.)

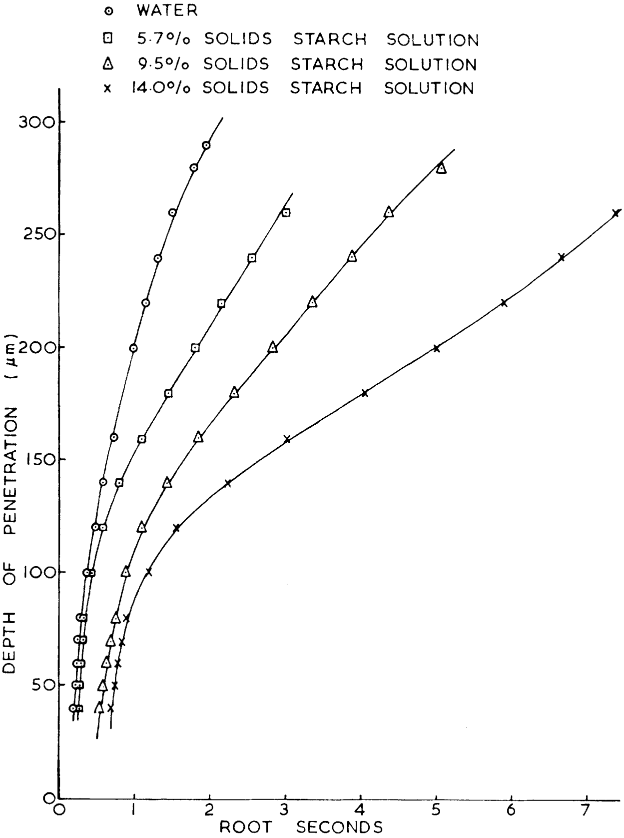


Fig. 13—Penetration curves for water and starch solutions, 54° SR base paper

The wetting time has been found to depend upon the roughness of the base sheet and the viscosity of the penetrating solution. The dependence on sheet roughness is illustrated in Fig. 14. Water appears to be unaffected by roughness, but, as the solids content of the starch solution is increased and with it the viscosity of the solution, then the dependence on roughness becomes increasingly significant. With relatively high viscosity solutions, the wetting time is influenced by the flow properties of the penetrating solution. This effect is demonstrated in Fig. 15.

According to the Lucas-Washburn equation, the slope of the depth versus root time curve is equal to $(r\sigma \cos \theta)^{\frac{1}{2}}/2\ \eta$. The initial and final rates of penetration were measured from the root time plots and examined in the light of

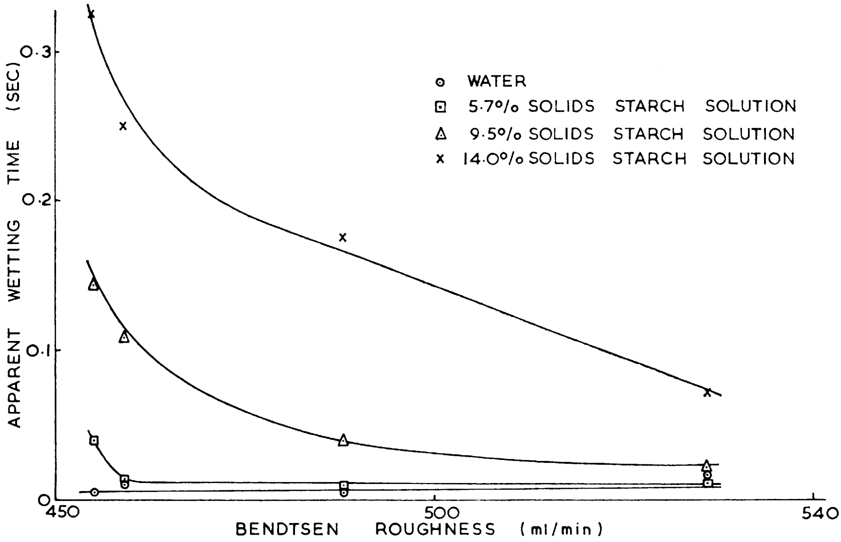


Fig. 14—Apparent wetting time against Bendtsen roughness

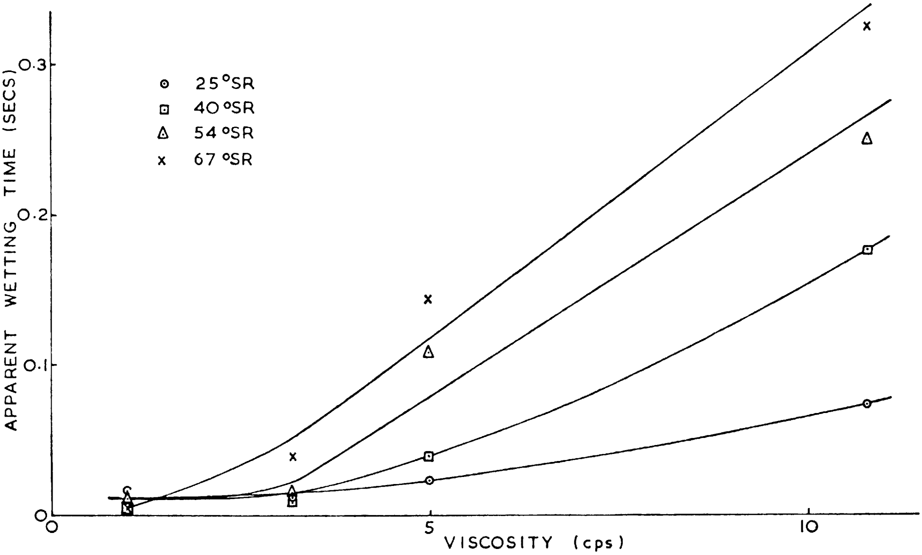


Fig. 15—Apparent wetting time against viscosity

Lucas-Washburn. Fig. 16 shows the ratio of surface tension to viscosity and the mean pore radius plotted against the initial slope squared. The mean pore radius was measured by using Corte's dioxane method. The same parameters

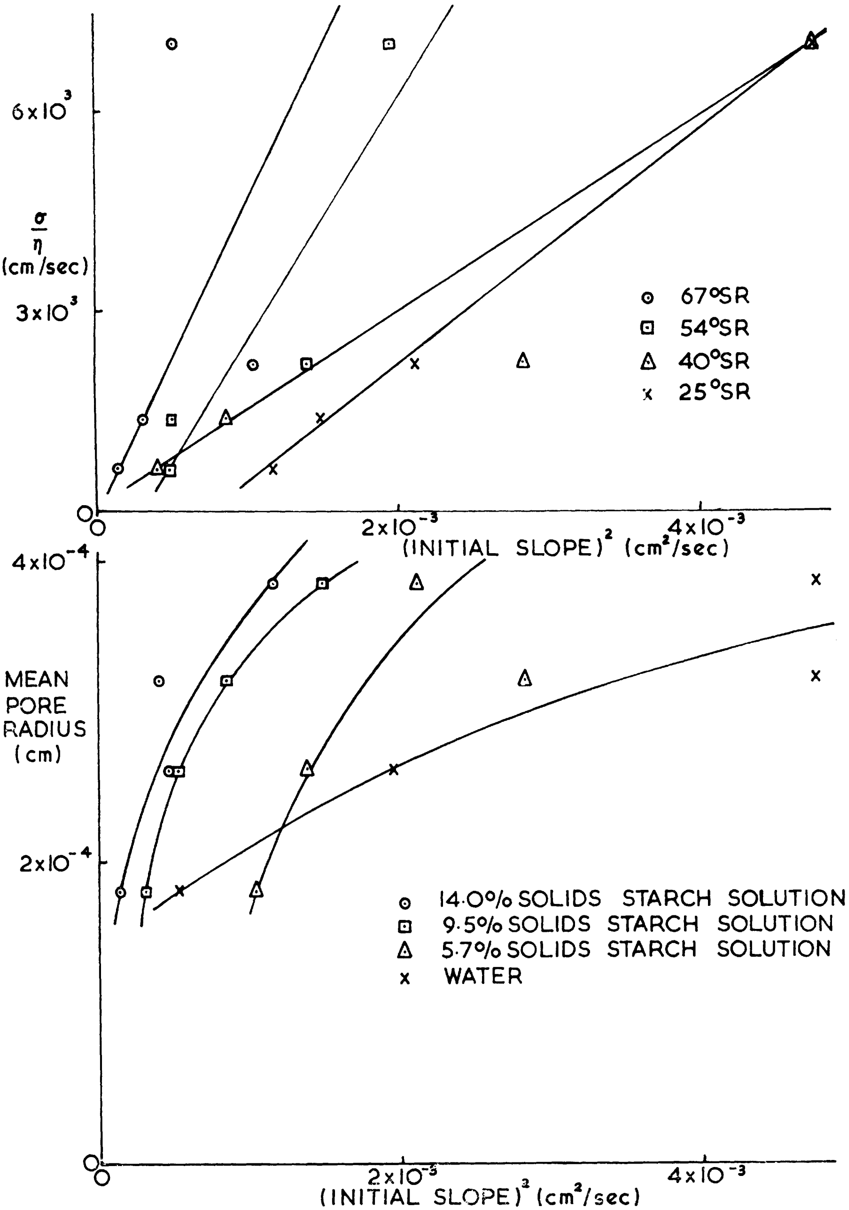


Fig. 16—Surface tension/viscosity and mean pore radius against (initial slope)^2 of root time curves

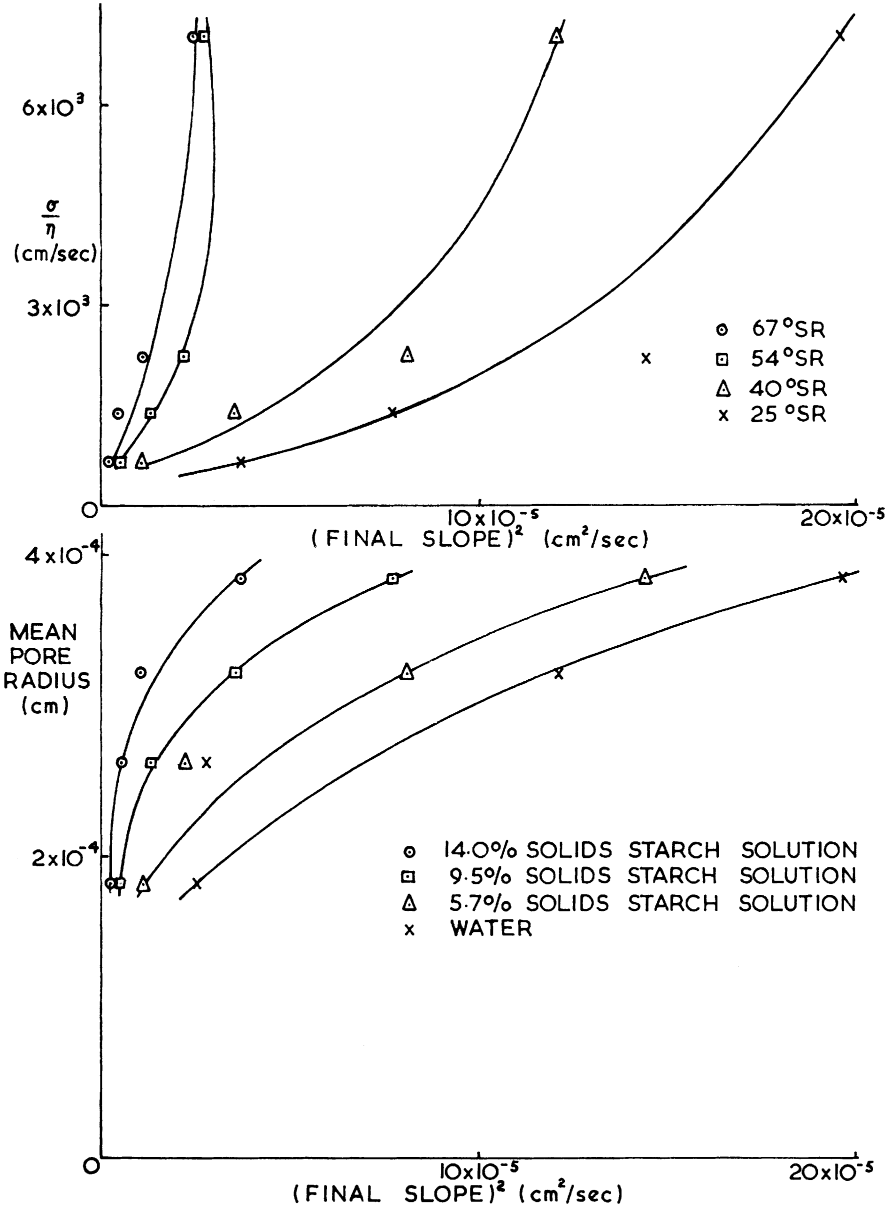


Fig. 17—Surface tension/viscosity and mean pore radius against (final slope)^2 of root time curves

are plotted for the final slope of the penetration curve in Fig. 17. In both cases, some form of relationship appears to exist, although the straightline relationship predicted by the Lucas-Washburn equation is not obtained for either part of the penetration curve.

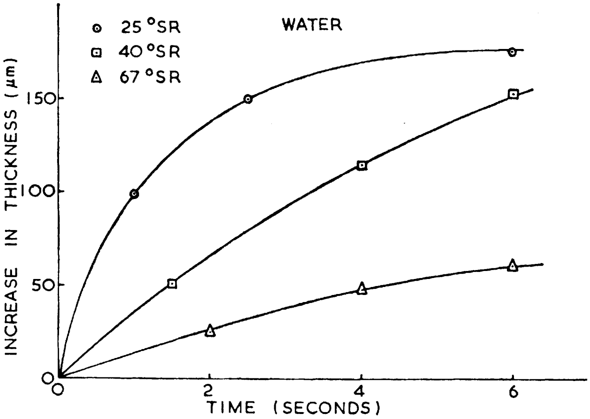


Fig. 18—Increase in thickness against time curves for water

It is believed that the reason for this deviation from the Lucas-Washburn equation is primarily due to neglect, in the derivation of the equation, of the swelling of the sheet that occurs as penetration takes place and the following model is offered. After the liquid has wetted the surface of the sheet, it is absorbed into the fibres and penetration proceeds along the pores. Liquid is also absorbed through the walls of the pores. This results in a change in thickness of the sheet ΔZ and the depth of penetration is less than what would result if liquid were not absorbed into the fibres. The change in thickness as the sheet is penetrated is significant, as Fig. 18 and 19 for both water and 14·0 per cent solids starch solution show. A sheet made of nylon fibres with a small amount of highly beaten woodpulp added to the furnish in order to bind the sheet together was examined using the penetration apparatus. The depth versus root time plot shown in Fig. 20 was obtained. The nylon fibres do not absorb water and a nearly straightline relationship resulted,

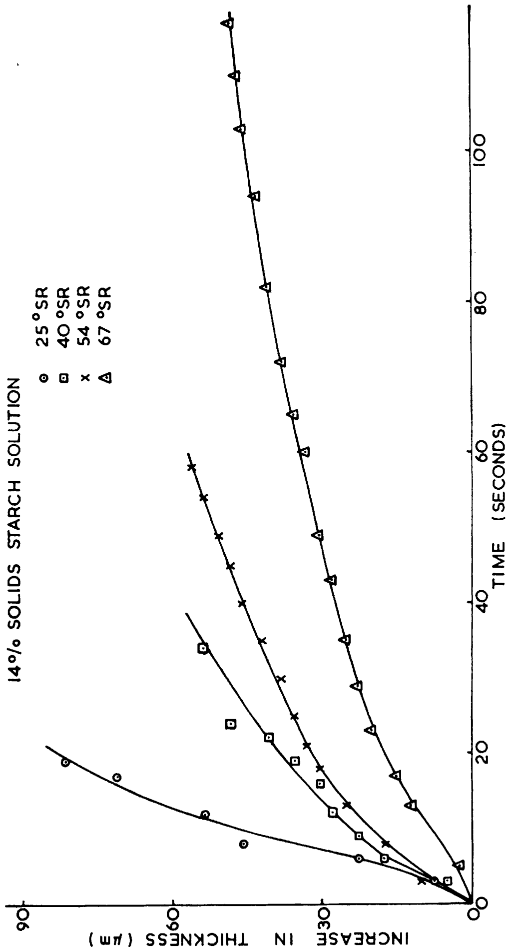


Fig. 19—Increase in thickness against time curves for 14 per cent solids starch solution

indicating that the swelling mechanism proposed above is important with wood fibres.

An equation of the following form is proposed for describing penetration after the wetting time—

$$l + k\Delta Z = (r\sigma \cos\theta t)^{\frac{1}{2}}/2\eta$$

where $l =$ depth of penetration after time t,
$\Delta Z =$ increase in thickness after time t,
$k =$ a constant.

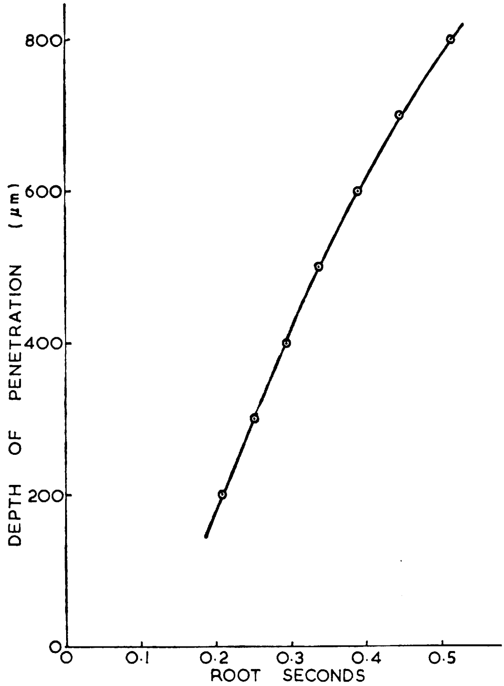


Fig. 20—Penetration curve for water with 75 per cent nylon/25 per cent 67° SR woodpulp base paper

This equation can be derived from a simple capillary model and results in the Lucas-Washburn term being equal to the measured depth of penetration plus a term $k\Delta Z$ to allow for swelling. Assuming $\cos \theta = 1$ (contact angle of zero degrees), the Lucas-Washburn term can be calculated and l and ΔZ have been measured. Therefore, a graph of the calculated depth of penetration minus the measured depth of penetration against the increase in thickness should give a straightline plot. Two such plots for water and 14·0 per cent solids starch solution are shown in Fig. 21 and a reasonable degree of linearity is obtained.

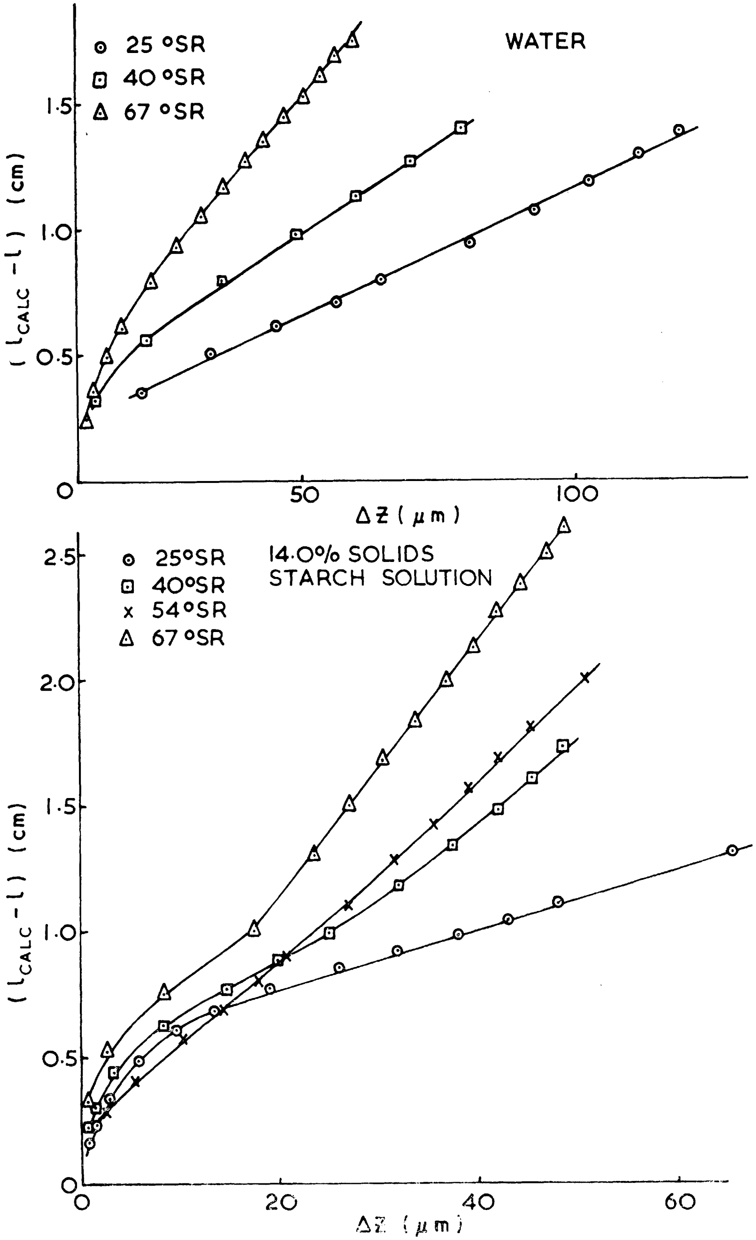


Fig. 21—Graphs ($l_{calc}-l$) against ΔZ for water and for 14·0 per cent solids starch solution

Coating mixes

Two clay/starch coating mixes have been examined using the penetration apparatus. The dispersant used was Calgon. Starch was added in appropriate proportions to give two mixes containing respectively 12 per cent and 18 per cent binder on the weight of clay and a total solids of 54 per cent. The depth of penetration versus time curve for the mix containing 18 per cent binder is shown in Fig. 22. A starch solution corresponding to the liquid phase for the mix containing 12 per cent binder was examined both with and without the addition of Calgon. The same base paper was used in all cases, being beaten to 54° SR with no sizing or other additives. Depth of penetration versus time curves were drawn and from these curves a plot of depth of penetration

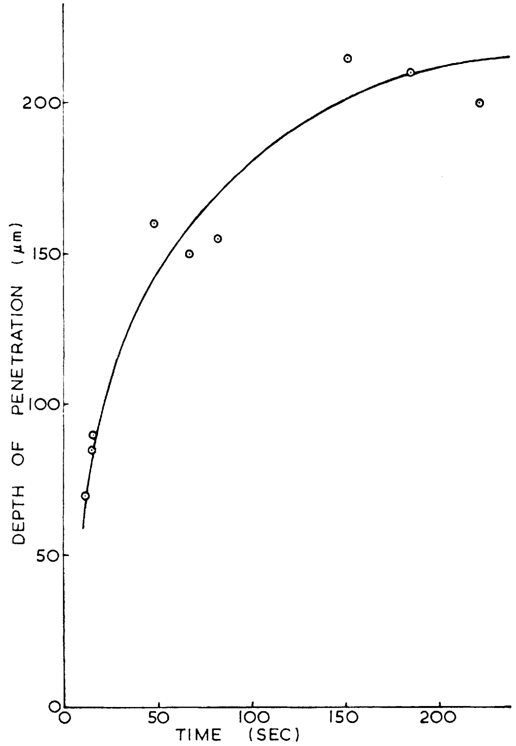


Fig. 22—Depth of penetration against time curve for 54 per cent solids, clay/starch mix, 18 per cent binder, 54° SR base paper

versus root time was obtained. The plots for the clay mixes are shown in Fig. 23 and Fig. 24 shows the results for the starch solutions; water is also plotted for comparison. The curves for the clay mixes exhibit the same shape characteristics found for water and starch solutions. Clearly, the effect of clay in suspension in the starch solution is to slow down the penetration of fluid into the sheet. The rate of penetration is much slower for the coating mix, hence it is probable that small clay particles are being carried along with the starch. The larger clay particles, by virtue of their size, being unable to enter the porous structure of the sheet would be retained and packed on to the surface of the sheet. Taking figures for the 200μ depth, with starch

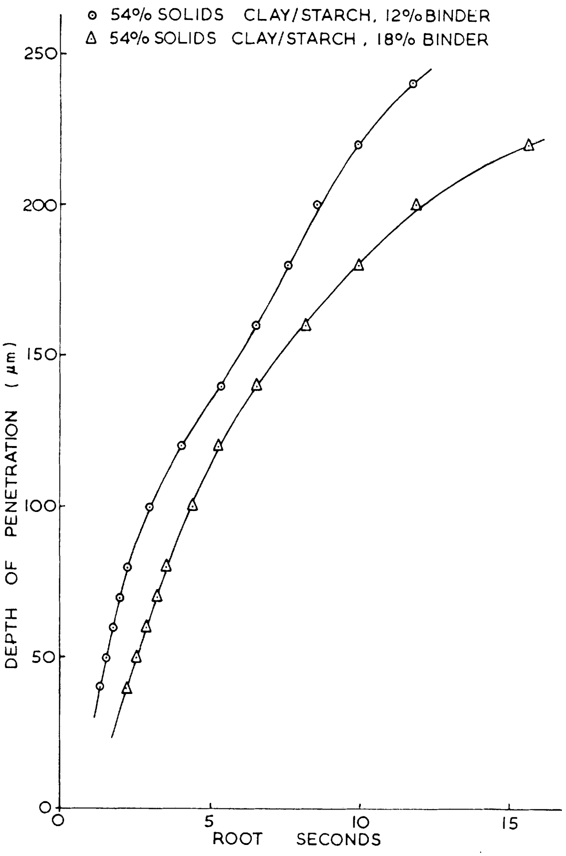


Fig. 23—Penetration curves for clay/starch mixes

and Calgon alone, the time to reach this depth is 9 s; with the clay added, the time for the depth of penetration is 49 s or so. The effect of the clay is very significant.

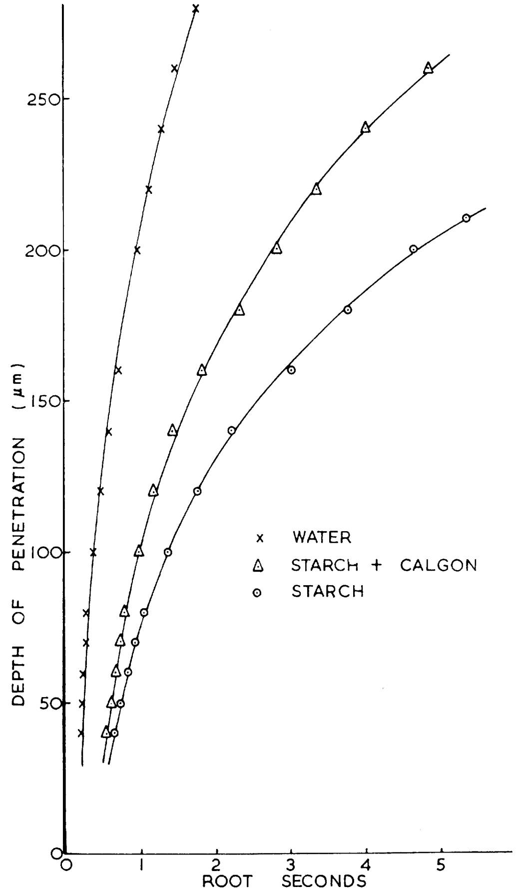


Fig. 24—Penetration curves for water, starch solution and starch solution plus Calgon

The penetration of a clay/latex mix and a clay/starch mix, both at 50 per cent solids, are compared in Fig. 25. Penetration is much faster for the clay/latex mix, owing to the much lower viscosity of this mix when compared with a clay/starch mix of the same solids.

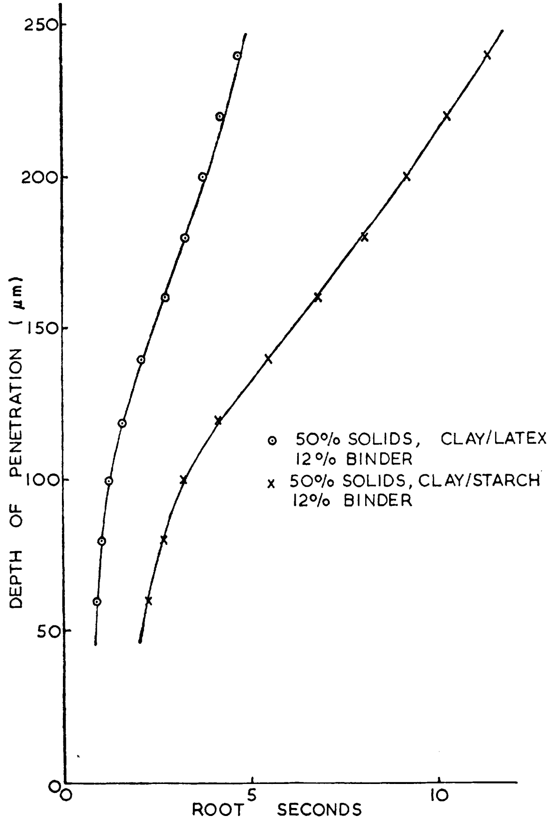


Fig. 25—Penetration curves for clay mixes, 54° SR base paper

Conclusions

THE theoretical work done in the analysis of the results reported here yields a penetration equation of the form—

$$l = \frac{(\sigma r \cos\theta)^{\frac{1}{2}}}{2\eta}(t-tw)^{\frac{1}{2}} - k\Delta Z$$

This introduces two new terms, *tw* the wetting time and *k* a dimensionless constant. (ΔZ also depends on time, but is measurable for any paper.) The wetting time has been shown to depend on sheet roughness and viscosity of penetrant. Since, in high speed coating, high viscosity of penetrant and short contact times may go hand in hand, a closer investigation of *tw* and, in particular, its dependence on sheet properties would seem a most useful line to follow in our future work.

Acknowledgement

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Discussion

Dr H. G. Higgins In these days of forming processes such as Wahren's, in which one tends to get three-dimensional structures rather than two-dimensional, I am a little surprised that more attention has not been paid to more appropriate relationships between porosity and permeability. At our meeting in Oxford 12 years ago, Mardon produced a little contribution from Scheidegger, which showed that the Kozeny-Carman equation had a dubious theoretical basis. An alternative approach in the Emersleben treatment, developed nearly 50 years ago, which expressed permeability in terms of the drag exerted on individual filaments. This was resurrected by Scheidegger in the first edition of his well-known book and, at Cambridge last time, we gave a paper to show that this treatment was to be preferred to the Kozeny-Carman equation for high porosity webs and that permeability could be related to structural anisotropy. My comment then is that we should perhaps give greater attention to methods of relating porosity and permeability, which are more appropriate than traditional approaches for the new papers derived from new forming processes.

Dr E. L. Back There was a significant difference between the methods reported today for evaluating absorption. The paper by Hoyland & Howarth, for instance, evaluated the depths of penetration (a parameter related to the effective pore size in the Z-direction), but the paper by Gate & Windle evaluated the amount of penetrating liquid at a given time (a parameter related not only to the effective pore size, but to a total number of these pores of effective pore size per unit area as well). These two methods do not rank papers in the same order. It is very easy to evaluate capillary rise and, in the same method, evaluate the amount taken up by this capillary in a given time. How do the authors relate their methods to the various end uses?

Mr P. Howarth Our work is concerned of course with the size press and coating equation, so we need more data on this penetration term. We found in a study of the literature that methods for measuring penetration either

Under the chairmanship of Prof. M. F. Judt measured the time for complete penetration or introduced some model between the measurements actually made and the interpretation of the results. We sought a direct measurement in which the readings of the instrument are directly related to the rate or depth of penetration. Clearly, if you want to turn this into a volume of penetration, then you have to multiply the depth by the area and porosity. This is the approach we would follow if we wished to do this.

Mr C. E. Dunning The first of my two comments refers to the wetting of the sample, in which there had apparently been oil absorption in the base sheet preceding the surface wetting by the oil droplet—the 'fingers' that were apparent ahead of the wetting interface could possibly be explained another way. If the oil in the underlying substrate has preceded the moving interface, it is possible that those fingers to reach out are simply doing so above oil-filled cavities in the substrate.

The second comment is somewhat philosophical in that surface chemistry equations consider in the rise of liquids in capillary structures only the equilibrium situation, they do not answer the question of just how those liquids rise. In other words, what are the physical mechanics by which the fluid pulls itself up into the column. My reaction to the film shown is that you appear to have a very beautiful technique for investigating the physical mechanics of liquid interface movement against a solid surface.

Mr J. F. Oliver To answer the first point, both absorption and spreading are occurring simultaneously and one could not really isolate in the technique used which was the important phenomenon. If I had more time, I could show some studies on model pore systems, such as films of a highly monodispersed latex, in which simultaneous surface spreading and some penetration into the open interstices occur. As a result, the latter largely determines the surface phenomena. In the example of the coated paper shown, the conclusion I made was based on the general effect that the pigment in the coating material presented areas of relatively higher surface free energy (Fig. 4), giving rise to local protrusions. At the same time, owing to absorption into the material, one could get further progress of liquid beneath the surface. Consequently, it might extend relatively further beneath the surface thereby influencing surface spreading by capillary attraction of the liquid absorbed.

In dealing with such a complex problem as shown by the dynamic sequence on the porous nature of the paper, I have generally avoided consideration of porosity and concentrated more on the surface properties. From a clearer understanding of spreading on rough surfaces, one may then proceed to a consideration of the problem of penetration into pores.

Incidentally, I would like to question the use of the classical equations for porous systems. I am a little puzzled how we understand what a pore is. The few studies that I have carried out on rough surfaces demonstrate that irregularities in the surface (such as sharp features) create a variation in the local angle of contact.(1) It seems reasonable to believe that similar behaviour in irregular pores might arise and would question the implicitly assumed fixed angle of contact.

Dr H. Corte There is one minor point of an experimental nature. Dr Hoyland mentioned that he had examined the pore size distribution using the so-called dioxane method. This was published in the transactions of the 1957 symposium. Unfortunately, the evaluation indicated there does not belong to the method described in the text, but to a variation of it. Unless the correct method of evaluation is used, the results would be quite wrong.

Dr R. W. Hoyland The method used to calculate the pore radius distribution was your corrected method of calculation. It gives a figure to substitute in the Lucas-Washburn equation, though we do not believe this is an absolute value.

Mr J. R. Parker May I make a comment about the spread of fingers of liquid along the fibre apparently following the ridges. This working phenomenon was predicted by Johnson & Dettre several years ago in a theoretical study of contact angle hysteresis. There is a reference to this in my paper to be given tomorrow.

Prof. V. T. Stannett In a mixture, is there not some kind of fractionation and filtration—in other words, is the composition of the penetrant not changing? Is this taken into account in some way?

Dr Hoyland We have considered this and we believe that there must be some change in the composition going on. One indication with a coated mix, for instance, is that when you remove the sheet from the apparatus, take off the surface layer of the coating adhering to the paper surface for measuring the solids content, then the solids content has risen by some 4 or 5 per cent solids above that of the original coating mix. It shows that there is some sort of compacting mechanism, maybe even some filtration type effect on the surface.

Mr D. J. McConnell Could I just mention one or two things that happened when we tried putting our standard, but rather porous base paper through a size press with a high solids pigment coating mix. To start with, we could find no pigment on the surface at all, it had all fallen inside the sheet. If anything, we have separation of the pigment and the starch solution in that the pigment was trapped within the fibres of the sheet and the starch solution was squeezed out again. We came to the conclusion that we were working with a base sheet that approximated to a wirewool sponge and that it was not wetted by the coating that poured into the sheet above the size press nip and that any wetting, swelling or other phenomena happened on the other side of the nip.

Dr A. de Ruvo I would like to ask somebody here in the coating field if they have made any measurements of the mechanical implications of coating. Could anyone recommend the optimum coating process to improve stiffness in board?

Mr P. Howarth I cannot give a definitive answer to that question, but, if you are coating to increase stiffness, the adhesive you use is the most important component. It is on record that some of the acrylic adhesives, for example, do produce an increased stiffness, I think the effect is fairly small on board. This is not the way to tackle that particular problem.

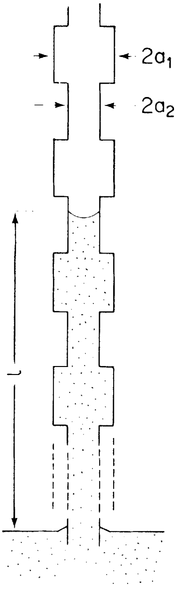

Fig. K

Discussion

Mr Parker We have spoken of the effective pore radius obtained from the Lucas-Washburn equation. I would like to point out that this radius is strongly affected by variation with length of the cross-section of the pore and that the original analysis given by Washburn was restricted to capillaries of uniform bore.

Consider a hypothetical capillary as shown in the diagram (Fig. K), composed of short segments of equal length, but having alternating circular bores of radii a_1 and a_2. If the effects of the abrupt changes of cross-section at the transitions from one diameter to another are ignored, it may be shown that the effective radius r that must be substituted into the following form of the Lucas-Washburn equation—

$$l = \left(\frac{\gamma r t}{2\eta}\right)^{\frac{1}{2}}$$

in order to predict the length l filled with fluid after time t is given by—

$$r = \frac{4}{({a_1}^3+{a_2}^3)({a_2}^{-4}+{a_2}^{-4})}$$

The following table illustrates how the effective radius may be very much less than either of the actual radii.

a_1	a_2	r
1·5	1·0	0·76
2·0	1·0	0·42
3·0	1·0	0·14

One has, therefore, to be a little cautious in interpreting the effective radius given by the Lucas-Washburn equation in terms of the structural characteristics of paper.

Mr L. F. Gate We mentioned this morning the Millington & Quirk method. They are in fact attempting to take into account a distribution for pore radii and I would rather like to hear what Dr Youngs thinks of the effectiveness of their treatment. Theirs is in fact an attempt to do what we have seen Mr Parker doing, only in a more general way; but in the literature (so far as I am aware), there seems to be very little use made of it. I would therefore like to know what an expert like Dr Youngs has to say about this method.

Dr E. G. Youngs As you probably are aware, my late Director, Dr E. C. Childs was very much concerned with this approach in its early stages. The difficulties in considering the flow properties through porous materials as Poiseuille flow are that you consider the flow through very short lengths of capillary tubes and we all remember that, when we measured viscosity with capillary tubes in our elementary physics classes, we always had to take end corrections into account. Thus, it always seems to me that, if you apply this sort of approach to get the flow properties of porous materials, there is an intrinsic error in that you assume Poiseuille's law to be obeyed in conditions in which it cannot apply.

We have long since given up the approach of obtaining permeabilities as given in the Childs & Collis-George paper. Millington & Quirk, also T. J. Marshall tried to improve the approach, but at best it is only an empirical one. I would merely add that it is very useful in obtaining values of the permeability if you have no direct measurements. In my experience, the measurement of the pore size distribution required for the computation is as difficult as measuring the permeability. I would prefer to do the latter than do the former.

In an earlier paper, the mercury intrusion method was mentioned. This is used of course because the contact angle fills the larger pores first. If a wetting fluid like water is used, as we usually do in soil studies, the smaller pores fill first and a rather different distribution of pores will be obtained because of different air entrapment.

I know of no visual measurements of pore size in porous materials for the conductivity.