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# FACTORS AFFECTING THE ABSORPTION TERM IN THE SIZE PRESS EQUATION

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**Synopsis** The equation for pick-up of surface sizes on the size press recently proposed by Hoyland & Howarth contains three terms. These are the immobilisation term and the absorption term, which are controlled by the sheet and the hydrodynamic term, which is primarily a function of speed. This paper describes pilot plant experiments to establish how the immobilisation and absorption terms are related to the various aspects of the sheet structure and composition. The most important factors were found to be structural differences associated with freeness changes and the presence of very small quantities of resin size. The latter were important at levels well below those associated with normal size addition.

#### Introduction

IN THEIR paper 'Fundamental parameters relating to performance of paper as a base for aqueous coatings',<sup>(1)</sup> R. W. Hoyland & P. Howarth discussed their size press equation, which describes the pick-up of surface sizes such as starch. The equation has three terms, of which the immobilisation term  $K_1$  and the absorption term  $K_2$  are found to depend on the structure of the base sheet before the size press. They then go on to discuss, in fundamental terms, the absorption of liquids into paper, primarily in terms of the Lucas-Washburn equation and of departures from it. The purpose of the present contribution is to record some experimental findings that relate to the influence of papermaking factors on pick-up of starch in size pressing, primarily through the adsorption and immobilisation terms.

#### Experimental results

THE investigation was made by Clarke & Wilson<sup>(2)</sup> using a pilot-scale horizontal size press. Unfortunately, at the time of this study, Howarth's size press equation was not available and so detailed analysis in terms of that equation was not made. Because the speed was constant and fairly slow, it is

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almost certain that the hydrodynamic term in the equation would have been small. Consequently, the factors found to influence starch pick-up must be the factors influencing one or both of the two terms—

$$K_1$$
 and  $\frac{K_2}{(\gamma S)^n}$ 

in the size press equation.

The first part of the investigation concerns paper from two mills each making a surface-sized pure body paper for airknife coating. Mill B did not achieve so high a pick-up of starch at the size press as did mill A and this was confirmed even more strongly when base paper from the two mills made without size pressing were treated on a pilot size press. Mill B then carried out two trials to imitate stock preparation and papermaking conditions at mill A. Considerable gains in starch pick-up were made, but did not reach mill A level. Differences in size press configuration were not the reason.



Absorbency (capillary rise), mm

Fig. 1—Relationship of base sheet absorbency to size press pick-up

It was found during this and other trials that the pick-up of starch on the pilot size press could be predicted from absorbency tests on the base paper before the size press (Fig. 1). The base papers were virtually unsized and therefore the conventional Cobb test was inadequate, so the capillary rise test for absorbent papers (PT16:pm 1947) was used and found to be very effective.

Samples from the papermaking trials were tested for absorbency by this method both as used and after extraction of rosin with alcohol to eliminate effects from rosin size. This procedure could of course affect other materials in the fibre, but the results are believed to be meaningful as a comparison,



Sample 1-Mill B base paper, normal making Sample 2-First trial at mill B, imitating mill A conditions Sample 3-Second trial at mill B, imitating mill A conditions Sample 4-Mill A base paper, normal making

The height of the unshaded column indicates the relative absorbency before the size press. The total height of the column indicates the absorbency that sheet structure permitted in the absence of rosin sizing. The shaded area indicates the degree to which the rosin sizing reduced the absorbency.

#### Fig. 2—Absorbency tests on machine-made papers

because similar pulps are involved throughout. The results are summarised in Fig. 2 and show that—

- 1. Mill B was able to achieve a similar sheet structure as was mill A in the trials, so far as parameters influencing starch absorption are concerned.
- 2. Mill B still had more residual rosin size than mill A (even though none was being added) and this prevented it from achieving the same size press starch pick-up. This is believed to be due to connected machine whitewater systems in mill B.

To investigate this further, a handsheet experiment was carried out in which base papers in pre-size press condition were prepared to a factorial design with beating (freeness), pressing, *small* rosin additions and furnish as independent variables. These were surface sized on the pilot size press by attaching them to a 'tail' to carry them through the machine. The results after analysis of variance are summarised in Table 1.

Condition	Estimated starch, per cent	Change in starch, per cent
Reference combination	5.6	
Change to 450° CSF and to the unsized condition	7.4	+1.9
Change to 450° CSF	6.7	+1.1
Change to unsized condition	6.6	+1.1
Change to mill B type furnish	4.8	-0.8
Change to nil wet pressing	5.9	+0.4

TABLE	1-RESULTS	OF	FACTORIAL	EXPERIMENT

#### Discussion

THIS work shows that pick-up of starch in a size press, in the region where the immobilisation and absorption terms of the equation are dominant, is influenced by sheet structural factors and by small quantities of surface active materials such as rosin size, which are likely to affect surface tension and contact angle.

Of the structural factors, freeness was found to be very important, which confirm Hoyland & Howarth's results. Small changes in the amount of hard-wood pulp used had some effect; compaction by pressing had little influence.

#### References

- 1. Hoyland, R. W. and Howarth, P., *The Fundamental Properties of Paper Related* to its Uses (this volume), 464–491
- 2. Clarke, B. and Wilson, C. M. W., Paper Tech., 1968, 9 (3), T35-T37

### **Transcription of Discussion**

## 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 twodimensional. 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

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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.

#### Discussion

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.<sup>(1)</sup> 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—

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

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.

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.