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PRACTICAL ASPECTS OF PAPER/LIQUID INTERACTION DURING PAPER COATING

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Synopsis An attempt is made to demonstrate the relationship between paper as a substrate and the different properties of coating colours by photographs of microtome sections. The results are based on the coating technology of industrial and pilot plant experiences.

The first part deals with multi-roll application, mainly size press operation with starches and coating colours and makes obvious the penetration zone of the different aqueous coatings. The effect of different factors of the coatings (viscosity, starch modification, solids, paper smoothness, sizing degree of the base paper and machine speed) on the coating weight and the starch penetration have been investigated and demonstrated.

The effect of coating colour application and the use of airknife and blade applications is shown in paper sectioning pictures and the results are discussed.

Finally, the migration problem of the different binders is investigated, especially using intense hot-air drying.

These demonstrations by micrographs of paper sections show the possibility of making visible some parts of the mechanism of paper and liquid interaction during paper coating.

Introduction

DURING the last two decades, many papers have been written, both from theoretical and practical points[1–5] about the nature of paper coating operations. Usually, these are limited in their references to specific grades of paper or methods of application.

It is a very difficult task to work out a theoretical understanding of all the different chemical and physical reactions taking place during the aqueous treatment of paper. These reactions are even more complicated by the use of different application techniques.

In the following, an attempt is made to demonstrate the relationship between paper as a substrate and the different properties of coating colours.

Under the chairmanship of Prof. M. F. Judt together with coating technology based both on industrial and pilot plant experience.

Coating application

THE papermaker knows by experience what will happen when he makes minor changes to the base paper or coating colour composition, yet it is very seldom that there is a good theoretical explanation of the effects of these changes.

In the most common paper treatment operation—size press application—there are many variables that determine the coating weight and the penetration of the coating such as—

> Porosity, smoothness, sizing degree and compressibility of the base paper; the solids content, viscosity/rheology, water retention of the coating colour and the application conditions and drying facilities of the machine.

A full understanding of all these variables and how they interact is desirable from the papermaker's point of view. During the size press treatment of a fine paper or any other internally sized paper, the starch uptake will increase with (*a*) decreased internal sizing, (*b*) decreased smoothness and (*c*) increased machine speed. It is normally stated that an increase of solids concentration will increase the pick-up, but this is true only under certain conditions.

Solutions of highly modified starches are usually of low viscosity and the viscosity does not change much with increasing solids content: pick-up with them will increase with increasing solids. The viscosity of the starch solution determines to a large extent the pick-up and the lower the viscosity of the starch solution, the higher the pick-up and the higher the penetration of the starch.

The penetration depth of the starch solution has been determined by microtome sectioning technique. The starch is stained with iodine in this first micrograph.

The starch uptake of an unsized paper with high porosity and absorption (such as fluting medium) is determined in the same way by the viscosity of the starch solution. Increased machine speed means in this case a decrease in the starch pick-up. The absorption of the starch solution in the pond is decreased through the lower holding time of the paper in this pond. The starch uptake can be increased again by increasing the solids, provided the starch viscosity does not increase too much.

Penetration of starch solution into an absorbent paper will also depend on the application technique. In a size press treatment, starch solution of 8 per cent would normally penetrate an unsized paper as shown in Fig. 1.

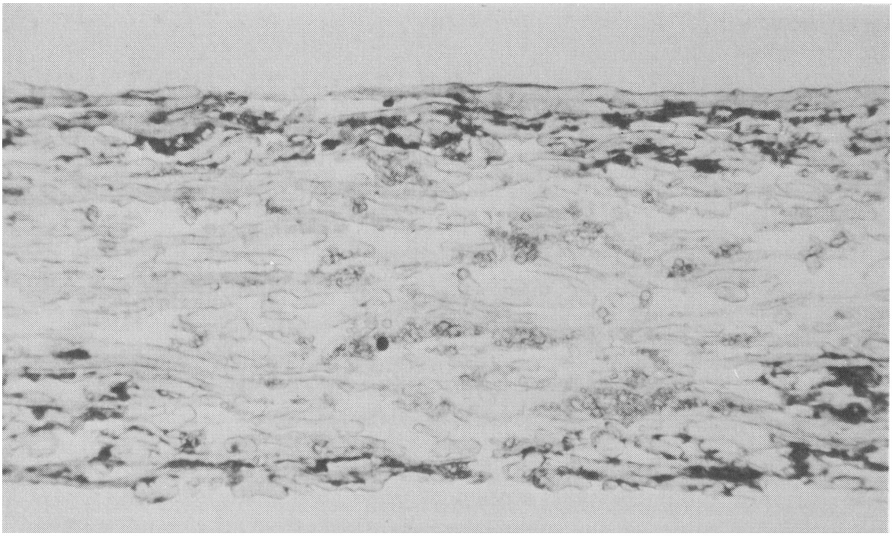

Fig. 1

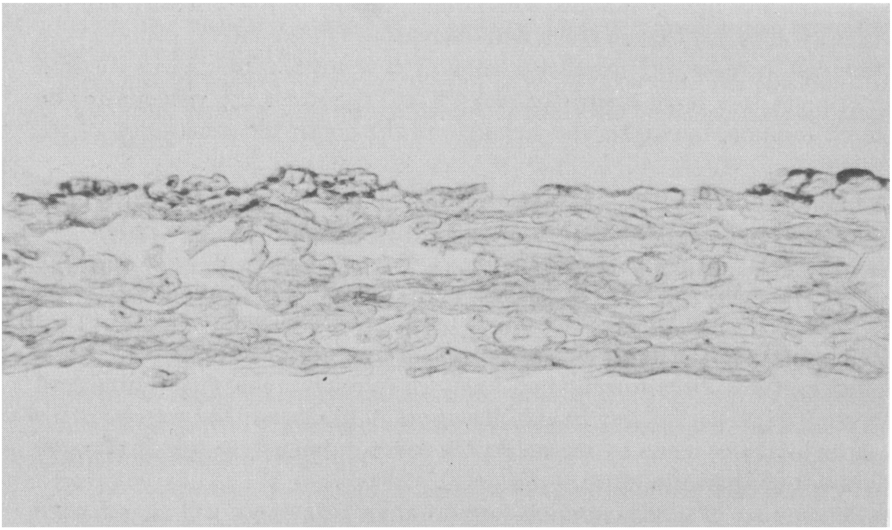

Fig. 2

When the same starch solution is applied in a gate-roll system, only a small quantity of starch is applied to the paper and there is no visible penetration (Fig. 2).

Without changing the machine conditions, but, on increasing the viscosity by raising the dry solids of the starch paste to 18 per cent, a thicker layer of starch is applied, resulting in greater penetration.

When the thickness of the starch film on the applicator roll is increased by changing the machine conditions, the starch will penetrate in the same way as by size press application.

The degree of penetration on different areas of the sheet will vary, however, depending on the absorption characteristics at these different areas, as seen in Fig. 4.

When coating colour is applied by means of the size press, the pick-up and penetration are influenced by other criteria than when starch solution is used alone.

The effect of the following factors on the coating weight and the starch penetration have been investigated—

1. Coating colour viscosity
2. Starch modification
3. Solids content of the colour
4. Paper smoothness
5. Sizing degree of the base paper
6. Machine speed

Lightly modified starches (such as oxidised starches of high viscosity) give coating colours that tend to stay on the surface of wood-free, very well sized, but very porous paper, as shown in Fig. 5.

Lowering the viscosity of the coating colour by the use of more highly modified starches does not influence the coating weight, but the penetration of the starch is increased (Fig. 6).

When the smoothness, porosity and at the same time the compressibility of the paper are changed by means of gentle treatment on a supercalender, the coating weight and starch penetration decrease as expected (Fig. 7).

One could expect that a paper with very low internal sizing and of lower smoothness than that of the paper in Fig. 7 would pick-up more coating colour and that the starch would penetrate more.

It is shown in Fig. 8 that it is not so. The coating weight decreased and the starch hardly penetrated the sheet. The reason for this unexpected behaviour is the lower porosity of this paper.

The coating weight is determined by the solids content of the coating colour and the base paper roughness, absorbency and compressibility. This absorbency cannot be measured using the Cobb test, as it devolves on the absorption rates while passing through the size press pond and this interval is very short —a second or less. The penetration depth of starch is determined by the

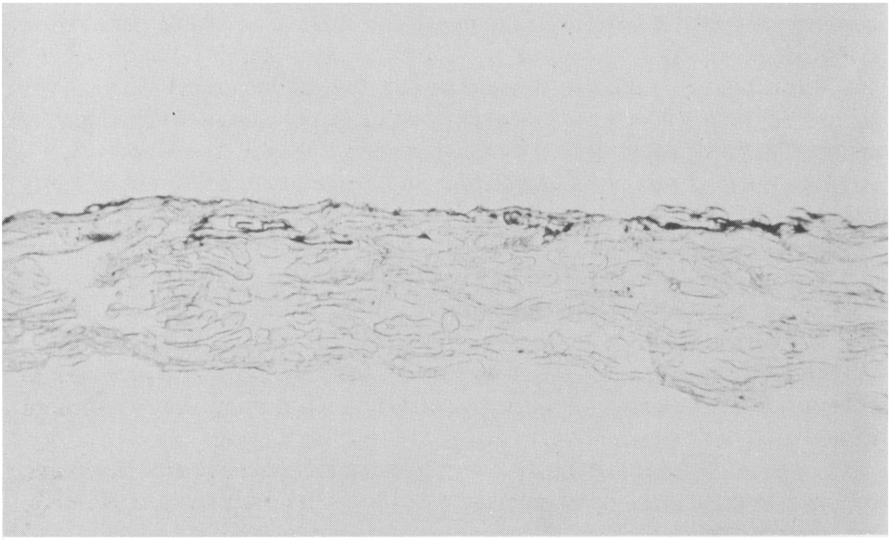

Fig. 3

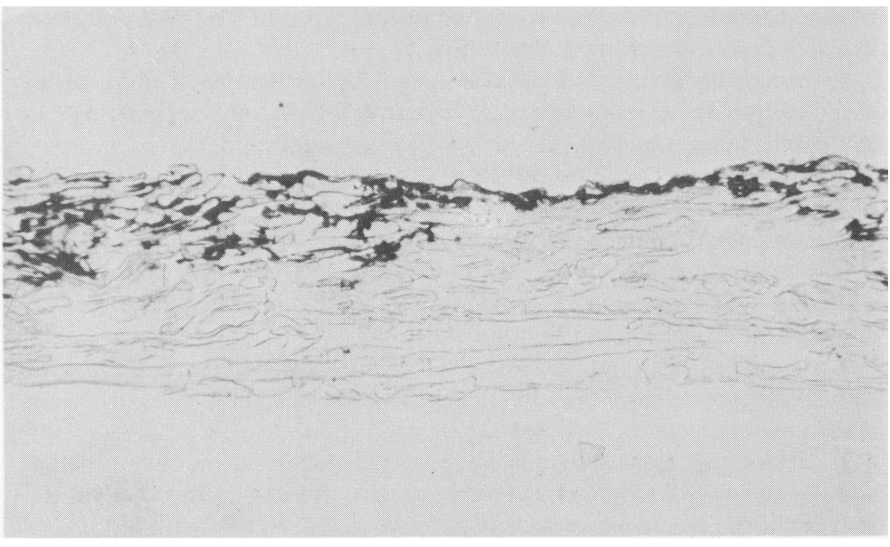

Fig. 4

degree of starch modification, the porosity of the base paper and the application technique.

The papermaker can only change the pressure between the size press rolls, as the runnability of the size press is determined by the viscosity and solids content of the starch solution or coating colour. At too high a viscosity, the coating colour will begin to splash; at too low a viscosity, the solids content of the colour might be insufficient to ensure the desired coating weight. This narrows the variables to—

1. Starch modification
2. Porosity/smoothness of the paper

The internal sizing of the paper also has an influence, but the paper is internally sized in order to give certain use properties to the paper independent of the size press operation.

The starch modification determines the solids level and so the pick-up and penetration are fixed. The porosity/smoothness is obtained from the furnish, degree of beating and wet pressing.

The moisture of the paper before the size press can be changed in order to modify the starch penetration, although this condition has always to be seen in relation to the final moisture content of the paper.

The speed did not influence the coating colour pick-up within 100–300 m/min. The orange peel effect, which normally occurs when the solids content is too high—and so determines the maximum solids content—was minimised by increased speed. Trials made with other paper grades showed that highly sized paper, with high smoothness (machine-glazed) tended to give more orange peel effect than did more absorbent papers.

In various trials, the water retention of coating colours for size press coating was found to have little influence on pick-up or penetration, though it has an important influence on the stability of the coating colour solids that circulate at the machine. How far the water/starch phase penetrates and at what rate the starch concentration decreases in the penetrating liquid is unknown. The distribution of *all* the starch cannot be determined by staining microtome sections with iodine. Low starch concentrations will not show up under the microscope, though the greater part can be located.

Until now, it has not been possible to determine a penetration zone of the binder when a coating colour is applied with a gate-roll coater.

Even a porous base paper can be given an even coating layer using this application technique (Fig. 9). The lower the porosity of the paper, the higher the degree of starch modification should be in order to achieve excellent bonding of the coating to the substrate.

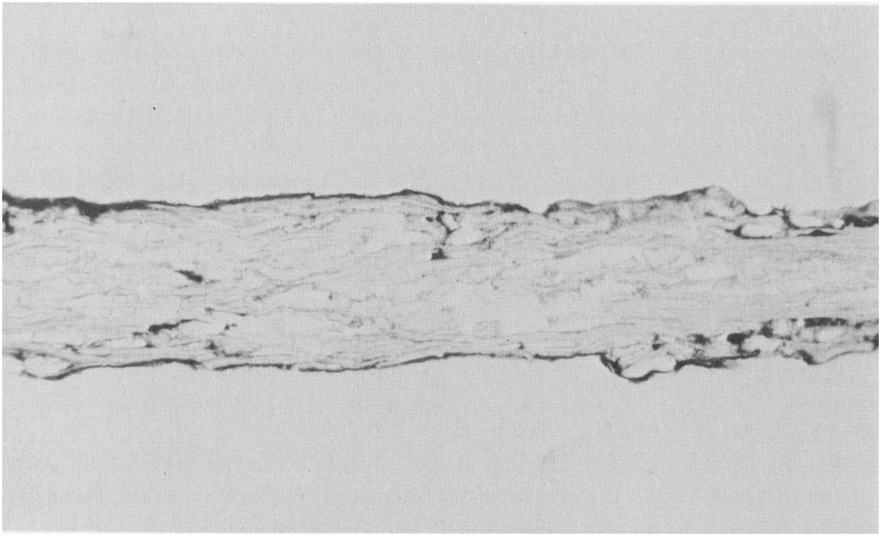

Fig. 5

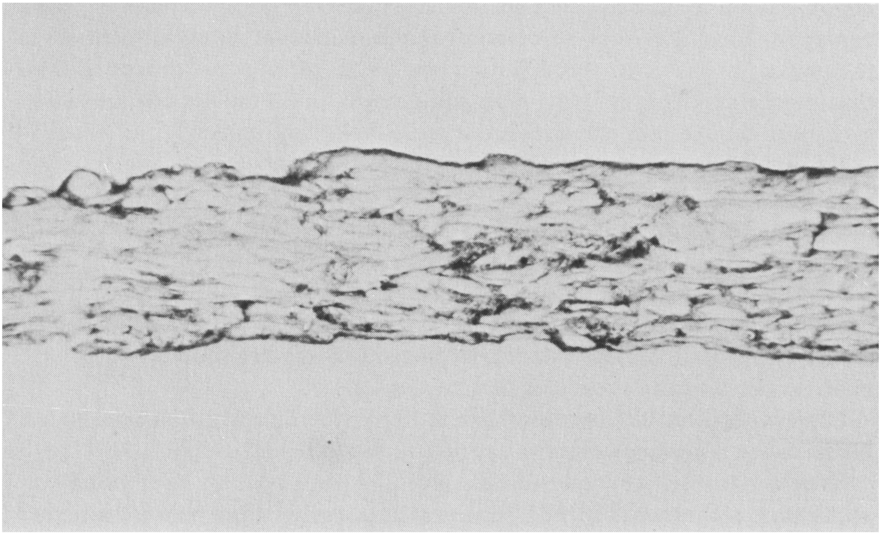

Fig. 6

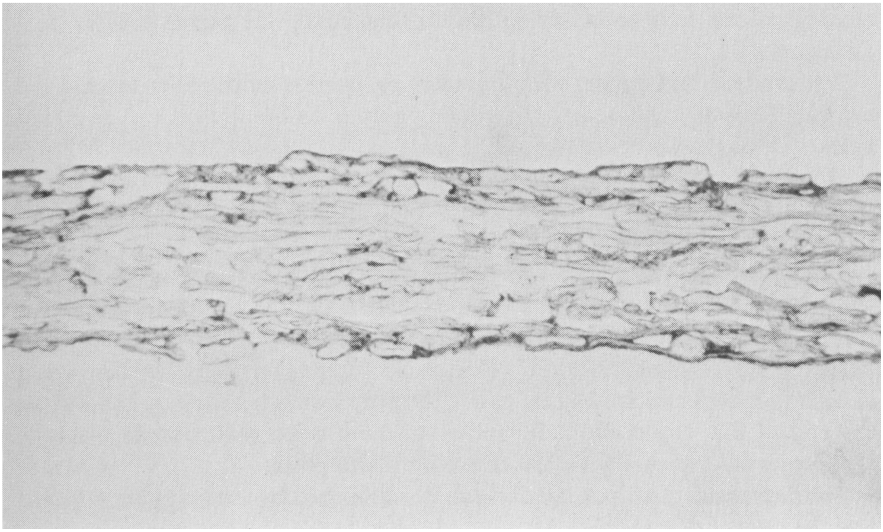

Fig. 7

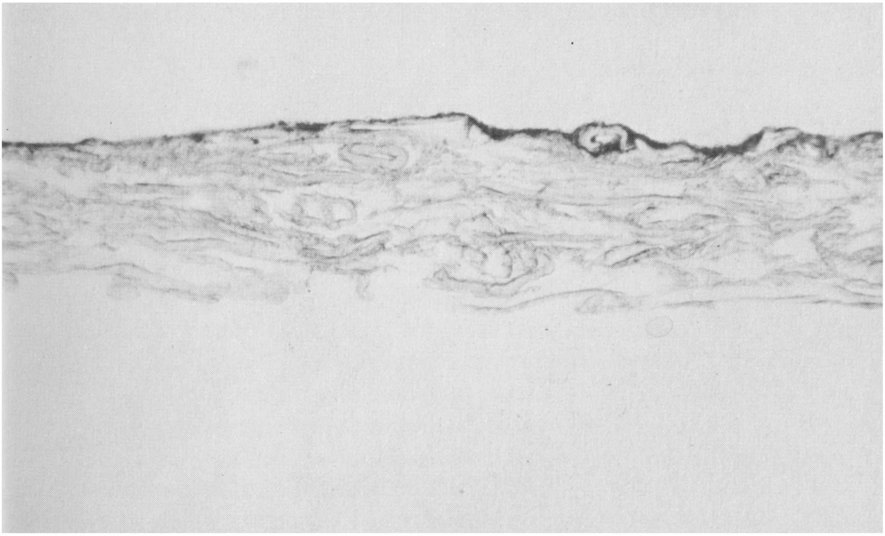

Fig. 8

With all measurements of base paper properties and the interaction with coating colour, it is necessary to reckon that nearly all papers exhibit two-sidedness.

It is obvious that papers with a greater proportion of the filler toward the top side (Fig. 10) will accept the coating colour differently on top and wire sides.

Good and even filler distribution (as seen in Fig. 11, with a titanium dioxide filled paper) should be achieved. This is difficult, but it should be possible by the use of good retention aids.

The difference in fine fibre distribution on top and wire sides also influences the performance of a coating base paper. The higher the filler content and the more fine fibres toward the top side, the lower the surface strength on this side. A surface sizing treatment will, of course, increase the strength of the weak side. It is more economical and easier to spray a starch slurry on the web at the end of the wire section. By spraying, there is no reduction in machine speed as would normally be the case with a size press.

The degree of starch penetration can be controlled by the spraying position and the danger of paper breaks is avoided by the use of a size press. Spraying is perhaps one of the easiest operations for improving (that is, decreasing) the absorption of coating colours. One disadvantage of this common operation to be mentioned is that until now only the top side can be sprayed.

Fig. 12 shows a microtome section of newsprint prepared for multicolour web-offset printing, sprayed with starch on the web in the wire section.

Use of blade and airknife techniques

BLADE coating is the fastest means of application today. At speeds of 800 m/min, very light papers (35 g/m^2) can be covered with a thin layer of coating colour.

Some fibres are hardly covered with coating (as is seen in Fig. 13) and it is expected that these areas should not reduce the print quality.

The base paper must be made of the cheapest possible materials and the quality must at the same time meet the requirements of high speed coating. Many different base papers were tried for lightweight coated papers on the pilot coater, of which some were excellent for this type of blade coating. Other papers with approximately the same measured physical properties as the good paper such as ash content, porosity, smoothness and sizing degree gave poor printing results, regardless of the coating colour applied.

It was found that the most important component of these papers was the quality of the groundwood used. A physical property, which is believed should be studied further in connection with high speed blade coatings, is the compressibility of the sheet.

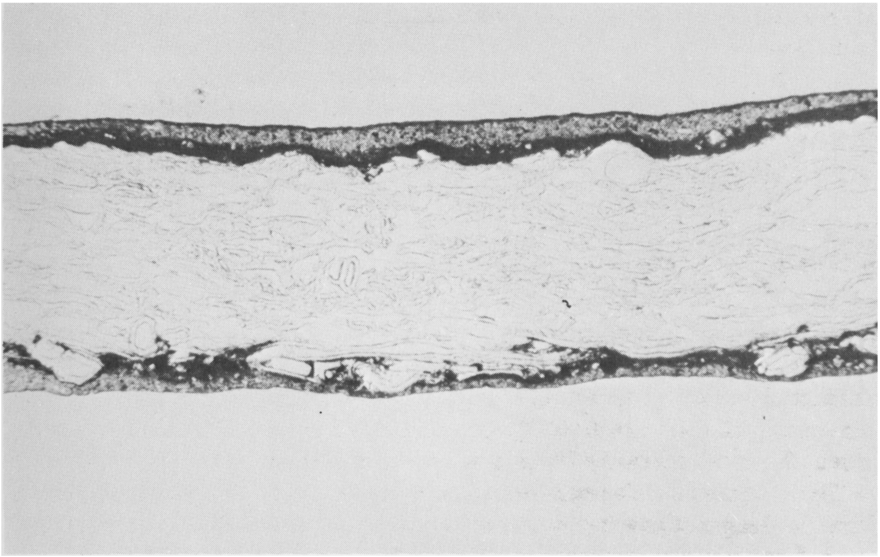

Fig. 9

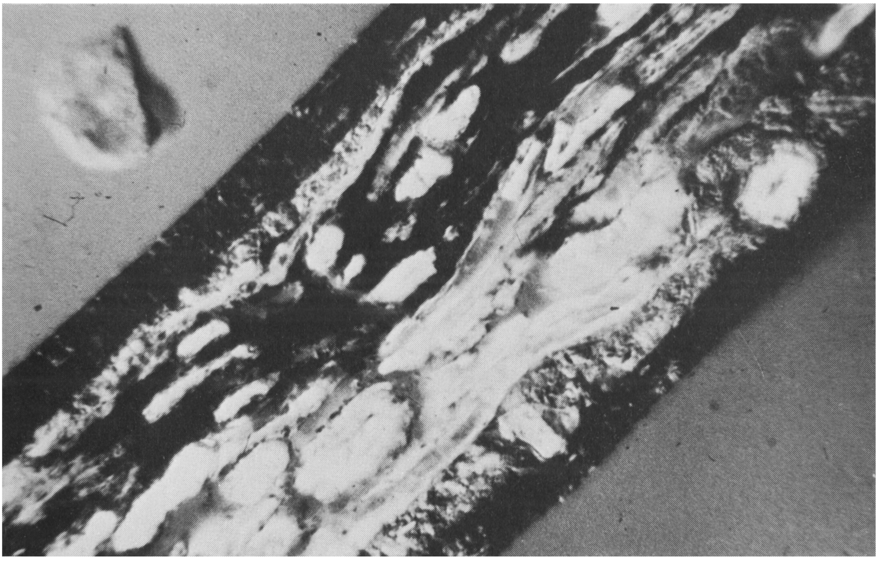

Fig. 10

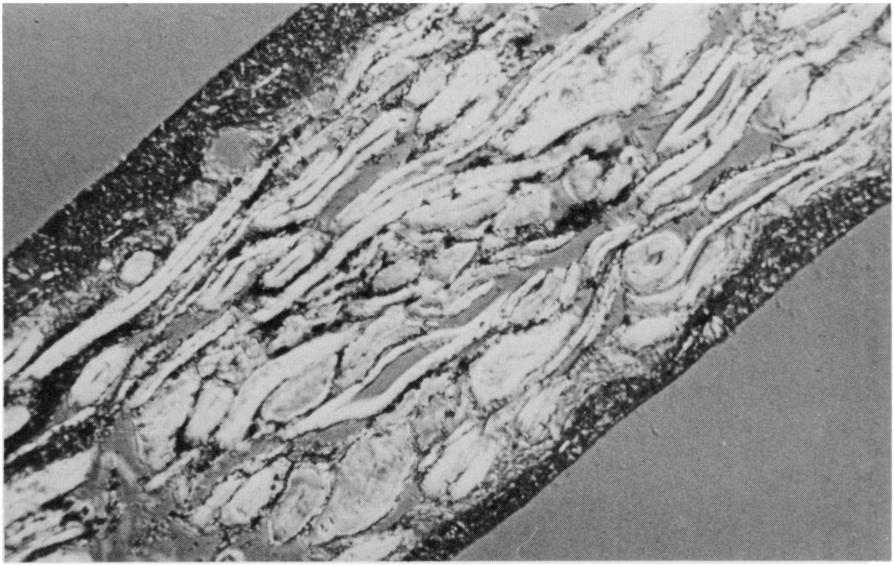

Fig. 11

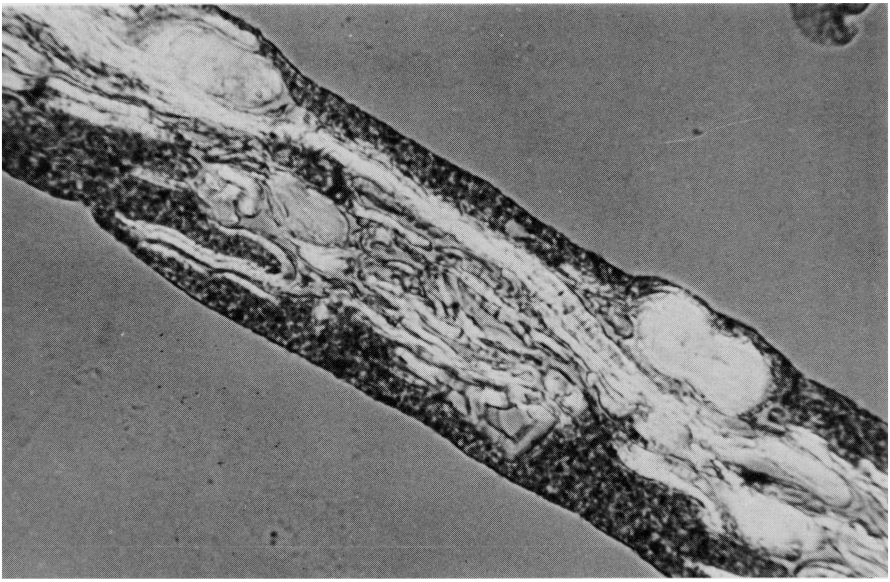

Fig. 12

For good runnability of such a paper on the coater, treatment with 1–2 per cent of wet strength resin is important. This treatment can prevent the coating colour fully penetrating the paper and dirtying the backing roll. Regardless of whether a 9 g/m^2 coating is applied on each side (Fig. 13) or 25 g/m^2 coating colour containing polyvinyl alcohol for speciality papers (Fig. 14), the solids content of blade coating colours should be greater than 55 per cent.

The binder demand in blade coatings is lower than for size press coatings or airknife coatings, for which the solids content is lower. The application and metering techniques in these three coatings methods, however, are quite different.

The coating colour is pressed into the paper between rolls of different hardness by the size press treatment. The pigment of the colour remains in the outer part of the paper and the starch solution penetrates further with the water, depending on the degree of modification of the starch and the base paper properties.

Airknife coating colours that contain natural binders have similar solid levels to those for size press coatings. The application and metering are carried out without any pressure or high shear of the coating colour.

The coating layer follows the contour of the paper and has the same thickness over the whole width (Fig. 15).

During the blade coating, there is a slight pressure of the applicator roll covered with coating colour on to the paper and backing roll, later by the blade action, when the coating colour is doctored off at very high shear rates.

Coating colour can be pressed into the porous substrate paper by the applicator roll. We have not been able, however, to find any penetration of binder, regardless of the quantity, into the base paper by airknife or blade coating operation. This is contrary to coating in the size press. There is no doubt that a very small quantity of binder—not detectable by microtome section staining technique—will separate from the pigment and migrate into the upper layer of the fibres;[6–10] otherwise, it would be impossible to bind the coating to the paper.

Migration of water and binder

THE water and binder migrates as a liquid face towards the substrate after the application of the coating. The pigment particles cannot migrate into the fibre network owing to the filtration effect. The liquid migrates only because of capillary forces. The molecules of the natural binder (in Fig. 16, this is starch) are absorbed by the cellulose fibrils and the binder concentration in the fluid decreases very rapidly. If this were not so, it would have been possible to make visible the penetration of the binders by microtome sectioning.

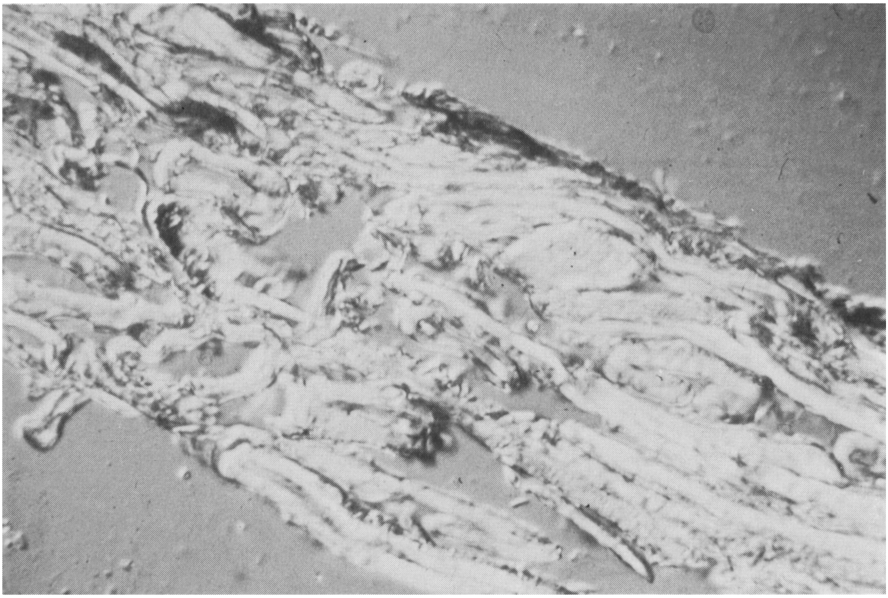

Fig. 13

Fig. 14

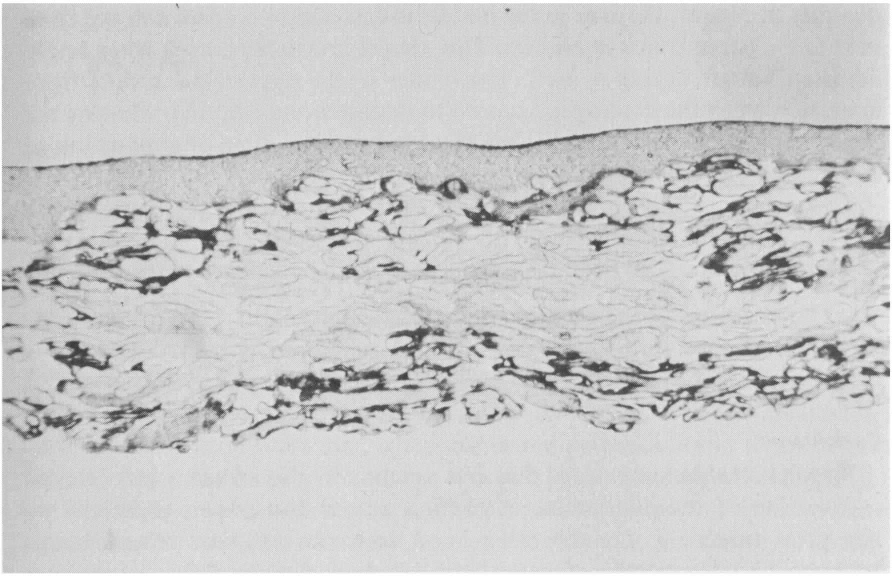

Fig. 15

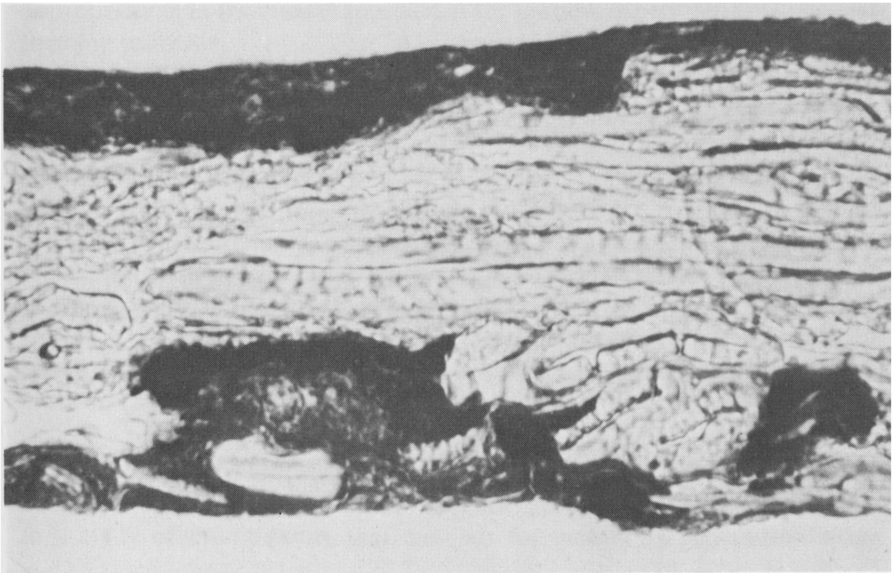

Fig. 16

Fig. 16 shows three zones in the coating. The upper zone contains a large quantity of binder; the area in the middle is depleted of binders and the zone next to the paper is rich in binders. This almost invariably occurs when badly adjusted hot-air drying is used. The binder in the upper zone results from migration when the coating is exposed to intense hot-air drying, whereas the penetration in the lower zone takes place between the time of application of the coating and the drying.

This results mostly in uneven binder distribution in the top layer of the coating and the surface, thereby producing a mottled effect after printing.

Mottling is increased by the following changes in base paper properties[11]—

1. Increased internal sizing
2. Decreased porosity
3. Decreased groundwood content

Conclusion

FINALLY, it should be stated that it is not easy to give an exact and detailed explanation of the interaction of coating colour and paper, especially by size press treatment. On the other hand, it is obvious that these demonstrations by micrographs of paper sections show the possibility of making visible some parts of the mechanisms.

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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 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.

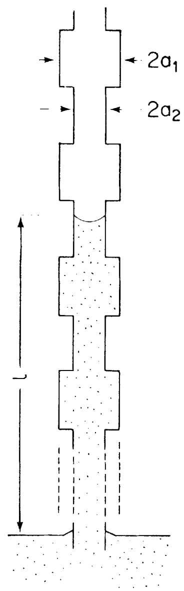

Fig. K

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.