

# EFFECT OF STRUCTURE ON MAJOR ASPECTS OF PAPER BEHAVIOUR WITH FLUIDS

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## **Synopsis**

*Firstly, the fundamental laws for the permeation, diffusion and penetration of fluids into porous material are explained and the available information on the porosity of paper is discussed. Using the classification in which neutral fluids like air, oil and grease are distinguished from those that interact with the pore walls like water and water vapour, the permeability to air and liquids like oil and grease is treated in greater detail. In addition to the description of the process of penetration, which is of special interest for printing inks, the main part of the paper deals with the behaviour of paper in relation to water and water vapour. Although the effect of swelling on porous structure has not yet been investigated sufficiently, some definite statements can be made on water and water vapour permeability. Furthermore, it is known how the moisture and the water content affect many properties of the paper, especially the strength.*

*Results of recent studies have been incorporated into the information already available. These investigations dealt with the penetration of water vapour into paper and the associated humidity and temperature effects. The paper closes with an account of some little-known studies on the effect of water vapour on paper and a general survey of dimensional stability and the tendency to curl.*

## **La relation entre la structure du papier et l'effet des liquides sur ses propriétés**

*En premier lieu, les lois fondamentales gouvernant la pénétration et la diffusion des liquides dans une matière poreuse sont exposées ainsi que les connaissances actuelles sur la porosité du papier. On fait*

ressortir la distinction entre les fluides neutres comme l'air et les matières huileuses et ceux comme l'eau à l'état de liquide ou de vapeur qui réagissent avec les parois des pores. On traite d'une façon plus détaillée le cas des liquides neutres, sujet d'un intérêt particulier dans l'étude de la pénétration des encres d'imprimerie. La plus grande partie de l'exposé est consacrée au comportement du papier en contact avec l'eau liquide ou à l'état de vapeur.

Bien que l'effet du gonflement sur la structure poreuse soit loin d'être mis au clair, certains faits concernant la perméabilité du papier à l'eau et à sa vapeur sont bien établis. De plus, l'effet de l'humidité du papier sur beaucoup de ses propriétés (et en particulier sur sa résistance mécanique) est connu.

L'ensemble des faits connus jusqu'à présent est complété par les conclusions de certaines études récentes. Ces études ont traité de la pénétration des vapeurs d'eau dans le papier ainsi que des effets associés de l'humidité et de la température.

L'auteur termine son exposé par un compte-rendu de certaines études jusqu'ici peu connues sur l'effet des vapeurs d'eau sur le papier. Celles-ci fournissent un exposé général des questions de stabilité dimensionnelle et de la tendance à l'enroulement du papier.

### **Die Wirkung der Struktur auf das Verhalten des Papiers gegenüber strömenden Medien**

Nach kurzer Erläuterung der Grundgesetze für das Durchdringen und Diffundieren strömender Medien durch poröse Stoffe und der Gesetze für ihr Eindringen wird das vorhandene Wissen über die Porosität des Papiers diskutiert. Eingeteilt nach neutralen Medien (Luft, Öle und Fette) und solchen, die mit den Porenwänden reagieren (Wasser und Wasserdampf) wird das Durchdringen dieser Medien durch das Papier im einzelnen behandelt. Nach der sich anschliessenden Erläuterung des Eindringprozesses, der besonders interessant für Druckfarben ist, beschäftigt sich der Bericht hauptsächlich mit dem Verhalten der Papiere gegenüber Wasser und Wasserdampf. Obwohl das Quellverhalten poröser Strukturen bis jetzt noch nicht ausreichend erforscht ist, lassen sich doch einige definitive Feststellungen machen. Ausreichend bekannt dagegen sind die Auswirkungen von Feuchtigkeit und Wassergehalt auf viele Eigenschaften des Papiers, besonders auf die Festigkeitseigenschaften.

Neuere Studien befassen sich mit dem Eindringen von Wasser-

*dampf in Papier. Den Abschluss bilden die Ergebnisse von Forschungen, die einen allgemeinen Überblick über die die Dimensionsstabilität und die Rollneigung der Papiere gestaltenden Zusammenhänge vermitteln.*

### Introduction

THE determining factor in the behaviour of paper under the influence of fluids is its porous structure and its hygroscopicity. In the case of gases like air and water vapour, as well as that of fluids like water, aqueous solutions, oil, grease, etc., penetration and permeation are always brought about by forces that rely on the porous structure of paper.

It would therefore be desirable to have an accurate knowledge of the nature of paper porosity and of the way in which certain fluids change it. The known laws for penetration, permeation and flow would then be sufficient to make all necessary predictions with certainty.

There are essentially two difficulties, however, that prevent a full interpretation of the facts. The first is a lack of knowledge of the exact nature of the porosity of paper. We should know not merely the number and distribution according to size of those pores that pass right through the paper, but the size, form and course of direction of all the pores in its structure.

It is known that any simplifying hypothesis—for example, assumption of a circular cross-section, a medium diameter or pore length equal to paper thickness—is incomplete. The other difficulty arises from fibre swelling, caused by fluids like water and water vapour, which affect the pores. The exact effect of this swelling on the penetration of fluids into the pores of paper has not yet been ascertained.

Despite these gaps in our knowledge, an attempt will be made here to outline the existing knowledge in this large and important field, starting with the fundamental laws by which the nature of the processes concerned can be explained in a general manner. This will be followed by a discussion of specific aspects of the problem, with the addition of some new findings.

## FUNDAMENTALS OF FLOW

### *Non-compressible fluids (water, oil, etc.)*

IF a steady state flow caused by a pressure gradient passes through a tube of circular cross-section, the Hagen-Poiseuille law for laminar flow applies—

$$V = \frac{\pi r^4 \Delta p}{8\eta l} \quad (\text{m}^3/\text{h}) \quad \dots \dots \dots (1)$$

where  $V$  = volume per unit of time ( $\text{m}^3/\text{h}$ ),  
 $r$  = radius of the tube (m),  
 $\Delta p$  = pressure drop ( $\text{kg}/\text{m}^2$ ),  
 $l$  = length (m),  
 $\eta$  = viscosity ( $\text{kg h}/\text{m}^2$ ).

The mean velocity of flow  $v$  is expressed by the equation—

$$v = \frac{r^2}{8\eta l} \text{ (m/h)} \dots \dots \dots (1a)$$

The laminar flow changes to turbulent flow, if the Reynolds number  $Re$  exceeds 2 300.

$$Re = \frac{vd}{\nu} = \frac{vd\rho}{\eta} \dots \dots \dots (2)$$

where  $d$  = characteristic length (m),  
 $\nu$  = kinematic viscosity ( $\text{m}^2/\text{h}$ ),  
 $\eta$  = dynamic viscosity ( $\text{kg h}/\text{m}^2$ ),  
 $\rho$  = density ( $\text{kg h}^2/\text{m}^4$ ).

The following equation for liquid flow through incompressible porous media (that is, for more complex systems) was established by Kozeny<sup>(1)</sup> and later modified by Carman<sup>(2)</sup>—

$$V = \frac{\epsilon^3}{kS_0^2(1-\epsilon)^2} \cdot \frac{F}{\eta l} \Delta p \text{ (m}^3/\text{h)} \dots \dots \dots (3)$$

The term  $\epsilon^3/kS_0^2(1-\epsilon)^2$  represents a constant for a penetrated porous medium; this constant is called the permeability coefficient  $K$ , where—

$\epsilon$  = proportion of the pore volume to the total volume,  
 $k$  = constant dependent on the material of the medium,  
 $S_0$  = specific surface of solid material per unit volume ( $\text{m}^2/\text{m}^3$ ).

The permeability coefficient  $K$  can be determined by a flow test from the relationship—

$$K = \frac{\eta l V}{F \Delta p} \text{ (m}^2) \dots \dots \dots (3a)$$

where in equation (3) and (3a)—

$F$  = penetrated total cross-sectional area of the medium ( $\text{m}^2$ ),  
 $l$  = thickness of the penetrated layer (m).

The permeability coefficient  $K$  indicates the rate at which a porous body under specified experimental conditions is penetrated by a liquid of

known viscosity. Therefore, it represents a characteristic value, useful for practical purposes.

**Compressible fluids**

WHEN applied to gases, the Hagen-Poiseuille law becomes—

$$V = \frac{\pi r^4}{8\eta l} \Delta p \frac{p_m}{p} \quad (\text{m}^3/\text{h}) \quad \dots \quad (4)$$

where  $p_m$  = medium pressure of the permeating gas,  
 $p$  = pressure at which  $V$  is measured.

The Knudsen law is used in the case of small absolute pressures, where the mean free path of the gas molecules is larger than the diameter of the capillaries—

$$V = \frac{4}{3} \sqrt{2\pi} \sqrt{\frac{R_0 T}{M}} \cdot \frac{r^3}{l} \cdot \frac{\Delta p}{p} \quad (\text{m}^3/\text{h}) \quad \dots \quad (5)$$

where  $R_0$  = universal gas constant (848 m kg/k mol °K),  
 $M$  = mass of one mole (kg h<sup>2</sup>/m k mol),  
 $T$  = absolute temperature (°K).

Compared with Poiseuille’s law for denser gases, the influence of the capillary radius is less; the factor of viscosity disappears completely and so does that of the medium pressure.

If the capillaries are very small, the mean free path of the gas molecules, even at higher pressures, may be of the same order as the capillary radii. In addition to laminar flow, governed by the Hagen-Poiseuille law, gas transport will be effected also by the so-called slip effect, where the wall layers play a part in producing movement. This process is expressed by the equation of Warburg, who describes the flow of gases through narrow capillaries as a laminar flow in a capillary of radius  $r' = r + \eta/\epsilon$ ,

where  $\eta$  = intermolecular friction, (kg h/m<sup>2</sup>),  
 $\epsilon$  = extramolecular friction (kg h/m<sup>3</sup>),  
 $\eta/\epsilon$  = coefficient of slip (m).

The Poiseuille law is now expressed by the following equation—

$$V = \frac{\pi r^4}{8\eta l} \cdot \frac{pm}{p} \Delta p \left(1 + 4\eta/\epsilon \frac{1}{r}\right) \quad (\text{m}^3/\text{h}) \quad \dots \quad (6)$$

The coefficient of slip, representing the ratio of intermolecular and extramolecular friction, is of the same order of magnitude as the mean free path of the molecules. Its influence is therefore noticeable only with capillary radii of the same order of magnitude as the mean free path.

**Diffusion of gases and liquids**

WHEN a mixture of gases (such as air and water vapour) or a chemical solution exists in a system at two places, with the absolute pressure equal at both places, but the partial pressures or the concentrations differing, Fick's law for diffusion applies.

For liquids at a steady state of diffusion—

$$V = -\frac{\delta F \Delta C}{l \gamma} \text{ (m}^3\text{/h)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where  $\delta$  = diffusion constant (m<sup>2</sup>/h),  
 $F$  = area of substance through which diffusion occurs (m<sup>2</sup>),  
 $\Delta C$  = difference of concentration (kg/m<sup>3</sup>),  
 $l$  = interval of diffusion (m),  
 $\gamma$  = specific gravity of the liquid (kg/m<sup>3</sup>).

For gases, provided the temperatures at both places in the diffusion system is constant, Fick's law is represented by the following equation—

$$V = -\frac{\delta F \Delta p}{l} \cdot \frac{1}{p} \text{ (m}^3\text{/h)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where  $p$  = pressure at which  $V$  is measured.

**Surface diffusion**

FICK'S law, however, does not cover a rather important phenomenon, surface diffusion, responsible for additional transference. The direction of movement of adsorbed molecules possessing two-dimensional mobility is determined by the gradient of the surface concentration along the path of diffusion.

The existence of surface diffusion was confirmed experimentally by Langmuir<sup>(3)</sup> and by Volmer.<sup>(4)</sup> Only a knowledge of the surface concentration of the diffusing medium (which can be determined by means of the adsorption theory of Brunauer, Emmet and Teller<sup>(5)</sup>) makes possible the calculation of these processes.

It was found that the quantity transferred by surface diffusion is negligible, so long as only a monomolecular layer exists. Only at concentrations indicative of polymolecular layer adsorption, where molecules in the upper layers are less strongly bound, does the transport of gas increase. In the case of fine-pored material, transport by surface diffusion can considerably exceed that calculable by Fick's formula.

Analogous to Fick's law the following equation can be established for surface diffusion—

$$G = -\delta U \cdot \frac{dc}{dl} \text{ (kg/h)} \quad . . . . . (9)$$

- where  $G$  = transported weight per unit time (kg/h),
- $U$  = width of path of diffusion (m),
- $\delta$  = surface diffusion coefficient (m<sup>2</sup>/h),
- $dc/dl$  = gradient of the surface concentration (kg/m<sup>3</sup>).

**Penetration by liquids**

WHEN liquids come into contact with a porous medium, penetration by capillary attraction often plays a more important part than does permeation.

If penetration proceeds in the absence of externally applied pressure, the rate of penetration depends on the three factors that determine the pressure in the capillaries—(a) surface tension, (b) wetting and (c) size of the capillaries.

According to Kelvin's law, the pressure  $p$  in the capillaries is given by—

$$p = \frac{2\sigma}{r} \cos \Theta \text{ (kg/m}^2\text{)} \quad . . . . . (10)$$

- where  $r$  = radius of the capillaries (m),
- $\sigma$  = surface tension corresponding to the system liquid/air (kg/m),
- $\Theta$  = contact angle between liquid and boundary wall.

Consequently, the contact angle (a measure of wetting) determines also the direction in which the capillary pressure is effective. For complete wetting ( $\Theta=0$ ;  $\cos \Theta=1$ ),  $p=2\sigma/r$ , pressure being directed into the capillaries. When the contact angle is 90°, capillary pressure is zero. When the contact angle is 180°,  $p=-2\sigma/r$ , repulsion occurs.

If a liquid penetrates from below into a vertical capillary and the latter is long enough, a maximum rise  $h$  is reached, at which equilibrium exists between capillary force and the weight of the liquid—

$$h = \frac{2\sigma}{r\gamma} \cos \Theta \text{ (m)} \quad . . . . . (10a)$$

- where  $\gamma$  = specific gravity of liquid (kg/m<sup>3</sup>).

In the case of horizontal penetration, the accelerating force is the product of surface tension and contact angle, with friction as the counteracting force.

The rate of penetration is calculated by using the accelerating force given in equation (10) and the friction as given in the Poiseuille equation (1a) as follows—

$$v = \frac{r\sigma \cos \Theta}{4\eta l} \text{ (m/h)} \quad . . . . . (11)$$

More general information is given by the Lucas-Washburn equation, which is obtained by integrating equation (11) over distance  $l$ —

$$\text{where} \quad l = \sqrt{\left[ \frac{r\sigma}{2\eta} \cos \Theta t \right]} \text{ (m)} \quad . . . . . (12)$$

$$\text{or} \quad l^2 = \frac{r\sigma}{2\eta} \cos \Theta t$$

If the equation is put as follows—

$$t = \frac{2\eta l^2}{r\sigma \cos \Theta} \text{ (h)} \quad . . . . . (12a)$$

it can be noted that the time  $t$  required for penetration into a certain capillary length  $l$  is proportional to the second power of this length and the viscosity of the liquid. Time of penetration decreases with increasing capillary radius, with increasing surface tension and decreasing angle of contact.

### THE POROUS STRUCTURE OF PAPER

IN most of the foregoing equations, the figure indicating the capillary radius will reveal the importance of the nature of the porosity for the processes of permeation and penetration.

The simplest and oldest explanation of the porosity of paper is the proportion of the void volume to the total volume of paper, which is calculated from the difference between the apparent density of the sheet and the density of the compact material. Apparent densities of paper without filler range generally from about 0.3 (blotting paper) and 0.5–0.7 (common papers) to about 1.4 (glassine),<sup>(6)</sup> whereas the density of the compact material is 1.5 (cellulose). From these figures, the percentage of the void volume is calculated, which is about 80 per cent for the bulky blotting paper, 70–50 per cent for paper of normal quality and about 5 per cent for the densest papers. These volumes comprise all pores. The volume occupied by the penetrating pores is, however, only a small fraction of the total pore volume, amounting to 1–2 per cent (maximum).<sup>(7)</sup>

More detailed information than that given above was obtained by tests to ascertain the qualities of the feature that determines permeability—the



mean radius of the penetrating pores. Carson<sup>(8)</sup> interpreted measurements of air permeability by means of Poiseuille's law, Simmonds<sup>(9)</sup> measured the capillary rise and Foote<sup>(10)</sup> used measurements of the contact angle, the capillary rise and swelling. Mean pore radii from  $1 \times 10^{-5}$  cm to  $4 \times 10^{-4}$  cm were found—that is, pore radii ranging in size from the light microscopical to the border of the colloidal zone. Vollmer<sup>(11)</sup> also found mean pore radii of  $10^{-5}$  to  $10^{-4}$  cm, when evaluating air permeability measurements at medium pressure by the Hagen-Poiseuille equation and measurements obtained at very small pressures by the Knudsen equation.

The behaviour of the whole porous system cannot, however, be assessed from a knowledge of mean pore radii only. A more comprehensive idea of the porous character will be obtained if, instead of the mean pore radius alone, a distribution of the pore radii over a larger range is taken into consideration. Tollenaar<sup>(12, 13)</sup> introduced a function of distribution for the pore radii, later Corte<sup>(14)</sup> and Mason and collaborators<sup>(15)</sup> employed experimental methods for determining distribution of pore sizes.

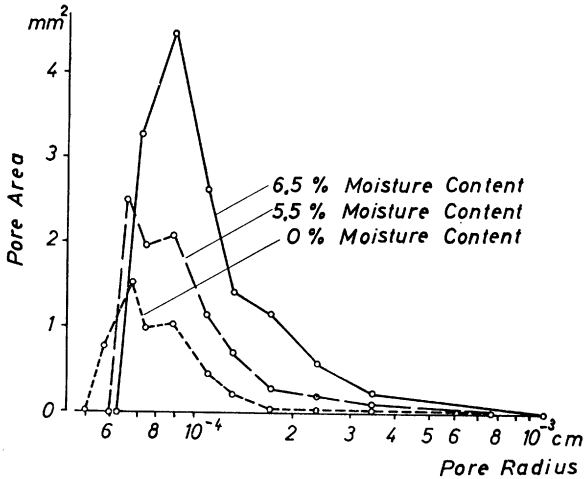
Corte<sup>(14)</sup> used the method for measuring pore size distribution described by Wakeham,<sup>(16)</sup> which had already been proposed by Ritter and Drake:<sup>(17)</sup> the paper sample is evacuated and mercury is forced into smaller and yet smaller pores under pressure, increased by predetermined grades. By applying Kelvin's equation, the pore radius corresponding to each pressure level can be calculated from the surface tension of mercury, the contact angle and the pressure. A pore distribution curve can then be obtained by graphical evaluation of the curve, which indicates for each pressure the increase in the volume of mercury that has penetrated into the pores.

The mercury method has certain disadvantages—the penetrating mercury fills the recesses as well as the pores and high pressures may cause all pores to expand. Corte, therefore, introduced another method in which the permeation of a gas (nitrogen) under gradually increasing pressure is observed: the paper is covered by and soaked in dioxane and the whole system isolated from the atmosphere. When this method was employed on greaseproof paper and vegetable parchment, it was established that the pores of the latter were smaller—about  $1.7\text{--}4 \cdot 10^{-5}$  cm compared with  $2.4\text{--}10 \cdot 10^{-5}$  cm for greaseproof paper.

In a series of measurements to study the influence of the moisture content of paper, small quantities of water were added to the dioxane (Fig. 1); Corte found that the pores enlarged as the moisture content increased.

Both the mercury and the nitrogen-dioxane methods give pore radii of the order of  $10^{-5}$  to  $10^{-4}$  cm. The shape of the curve for the pore size distribution is asymmetrical; it corresponds, however, to a normal Gaussian

distribution for the logarithm of the pore radius. The picture of the porosity of paper obtained in this manner is quite comprehensive no doubt, yet it is no more than a highly simplified model, supplying information only on pores penetrating the sheet completely, for which it assumes a circular, constant cross-section over the whole length of the pore. All other pores, representing a multiple of the volume of the penetrating pores, are disregarded,



**Fig. 1**—Pore size distribution of paper with different moisture content (Corte)  
(Zewa Lux, 62 °s.r., 80 g/m<sup>2</sup>, test area 16 cm<sup>2</sup>, measured with nitrogen in dioxane)

as are the real dimensions of the pores and their position in the paper. This simplified model is useful, however, when dealing with fluids that penetrate paper without changing the nature of the pores.

### BEHAVIOUR OF PAPER WITH FLUIDS

TABLE 1 (from Corte<sup>(14)</sup>) gives a classification of fluids, distinguishing between those that do not affect the structure of the paper and those that do so during permeation or penetration.

#### *Fluids without influence on paper*

##### *Permeation of gases*

Carson and others<sup>(18, 19)</sup> demonstrated that the Hagen-Poiseuille law for gases is valid for compressible fluids like air and Vollmer<sup>(11)</sup> has shown

TABLE 1—CLASSIFICATION

<i>Fluids</i>	<i>Effect on paper and its porous structure</i>	
	<i>Without</i>	<i>With</i>
Gases Mixtures	Dry air —	Water vapour Air containing water vapour
Liquids  Mixtures	Organic solutions grease, oil printing ink, varnish, etc.	Water  Grease containing water, varnishes

that Knudsen's law for gases works very well, provided the mean pressure is lower than 30 Torr.\*

Van den Akker<sup>(20)</sup> and before him, Lane,<sup>(21)</sup> on the other hand, found that more air permeates paper in the medium pressure range than was to be expected from Poiseuille's equation: even the slip effect, as taken into account by the Warburg law, is not quite sufficient to explain this phenomenon fully. Since the mean pore radius appears in the equations to the fourth power, there is no doubt that density, which exercises the greatest influence on the pore radii, determines the permeability to fluids like air. Several authors<sup>(22, 23)</sup> found that the permeability of a paper decreases with increasing density, resulting from a closer packing of long fibres or the presence of short soft fibres, but most of all, from beating of the stock and the pressing of the sheet. Nevertheless, a rather important problem—the influence of the moisture content of paper on the permeability of air—has not yet been solved. Carson and others<sup>(18, 24)</sup> have observed both increases and decreases in air permeability as the moisture content increases, without having found any indications of the underlying causes.

#### *Permeation and penetration by organic liquids (oil, etc.)*

The normal Poiseuille law applies to all liquids for which a steady state of capillary flow is concerned.

For the same *permeated* paper, therefore, the flow rate is dependent only on the viscosity of the liquid. According to Corte, the air permeability governed by the Poiseuille law can even be used as a quantitative measure of the grease resistance of paper, as there is a close relationship between the

\* Torr = mm mercury pressure at 0°C

frequency of certain large pores (which determines the grease penetration rate) and characteristic values of the pore distribution curve (which determine air permeability).

In the evaluation of grease resistance and many similar properties, the evaluation of the permeating volume at constant flow rate is far less important than the time elapsing before incipient penetration through the largest pores.

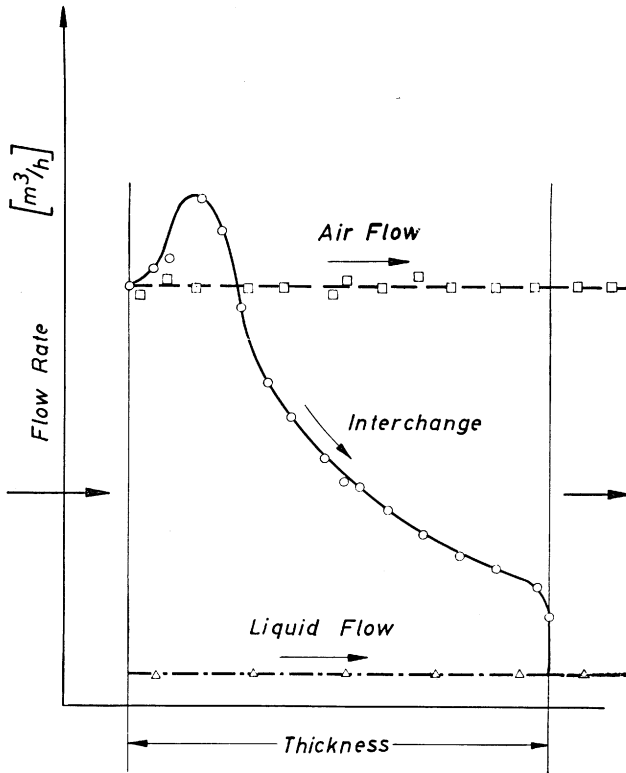


Fig. 2—Penetration and permeation (Corte)

For this reason, measurements worthy of note are those that establish the flow rate for the whole process of penetration and permeation by a neutral liquid. According to Corte, graphs of the kind shown schematically in Fig. 2 are obtained. At first, ahead of the penetrating liquid, air is expelled from the pores; when the liquid reaches the porous solid, capillary suction forces become operative and the rate of penetration increases sharply, after which the process is slowed down by friction until the pores are completely filled.

Experimental studies by various authors<sup>(25, 28)</sup> have shown that, for the *penetration* by liquids that do not affect the pore walls, the Lucas-Washburn equation, as previously explained, is valid to a first approximation—

$$l^2 = \text{const} \times t$$

where  $l$  = depth of penetration after time  $t$ .

This equation is valid when there is an excess of penetrating fluid and when the volume already penetrated is saturated with the fluid. Only then is there equal capillary pressure at each point.

If a concentration gradient exists within a penetrated zone, as often occurs (and can be observed, for example, when a single droplet is spreading), the capillary pressure in the penetrated zone is according to Gillespie<sup>(26, 27)</sup> no longer constant. The penetrated depth is in this case no longer proportional to the second power of the penetration time. The Lucas-Washburn law has lost its validity.

The direction followed by the fluid penetrating into the paper is of considerable importance for the rate of penetration as shown by Olsson and Pihl<sup>(28)</sup> for oil. When the direction is perpendicular to the plane of the sheet (that is, from one surface to the other), the penetration rate is lower than when it is in the direction parallel to the surface. The difference is much larger for calendered newsprint than for filter paper. This is probably caused in the first place by the calendering of the newsprint, which increases the density of the surface layer of the paper. In the direction parallel to the paper surface (that is, when spreading in the plane of the sheet), the velocity decreases with increasing angle from a maximum in the machine-direction to a minimum in the cross-direction.

Olsson and Pihl<sup>(29)</sup> also investigated the penetration rate of oil in papers sized to varying degrees. Unexpectedly, as the degree of rosin sizing increased, so did the penetration rate as measured by the penetration time. The air permeability of the paper increased at the same rate and the contact angle between the paper surface and water also increased.

This phenomenon of a rising oil penetration rate corresponding to the amount of rosin from the sizing was observed also by Carlsson.<sup>(30)</sup> It was attributed to increased porosity and a smaller contact angle between oil and paper—that is, to increased wetting. Furthermore, as found by Laroque<sup>(31)</sup> in some cases, the penetration rate of oil increases as the moisture content in the paper is raised.

During penetration of a heterogeneous liquid, separation of the constituents takes place; for example, in the case of printing inks—a mixture of

vehicle and pigment—the pigment does not penetrate as deeply as the vehicle.

The depth of penetration of vehicle and pigment has been studied microscopically by Coupe and Smith,<sup>(32, 33)</sup> who found that the depth of penetration of printing ink increases in direct proportion to the thickness of the film on the paper. For a given ink, the separation of pigment and oil depends primarily on the structure of the paper. The depth of penetration of the pigment is almost independent of loading. If the density of the paper is increased by calendering, the depth of penetration of the oil remains unaffected, whereas penetration by pigment decreases.

These empirically proved phenomena can probably be explained only by changes in the porosity of the paper and the contact angle for the system liquid/paper.

### *Fluids affecting the pore wall*

#### *Water*

*Permeation*—Permeation by water resulting from a pressure differential is of special interest for filter paper, in which a high permeability is required, together with good retention of solids and adequate resistance to bursting when wet.

For pressure conditions when the flow through the pores is not turbulent ( $Re > 2\ 300$ ), the Kozeny-Carman equation for permeability can be satisfactorily applied. The Eaton Dikeman Company<sup>(34)</sup> has established the permeability coefficient by means of a permeability apparatus and, from the results shown in Fig. 3, it can be seen that the coefficient of permeability is lowered as the pressure drop becomes greater, the decrease being greater for more permeable papers than for denser papers. The heavier pressures compress the wet web, thus decreasing the porosity.

The above-mentioned conditions, however, are valid only if the fibres can swell long enough for steady state conditions to be obtained. Swelling, whether caused by water or other swelling agents, leads to a reduction of the coefficient of permeability.

*Penetration*—Owing to absence of fundamental studies, there are as yet no definite theories regarding the mechanism of the penetration of liquids that cause swelling of the fibres and changes in pore structure connected with it.

Generally, the rate of penetration of such liquids is determined empirically with penetration meters commonly used for measuring the degree of sizing.

Seiler,<sup>(35)</sup> as well as Arledter,<sup>(36)</sup> investigated the penetration of aqueous

dispersions of varying viscosity and water content and found that penetration time increases with increasing viscosity. If the viscosity remains unchanged, while the water content increases, the penetration time increases; for an increase of the water content from 10 per cent to 30 per cent, it increases by 20 per cent.

The moisture content of the paper has a pronounced influence. If it increases from almost zero to about 4.5 per cent moisture, the penetration

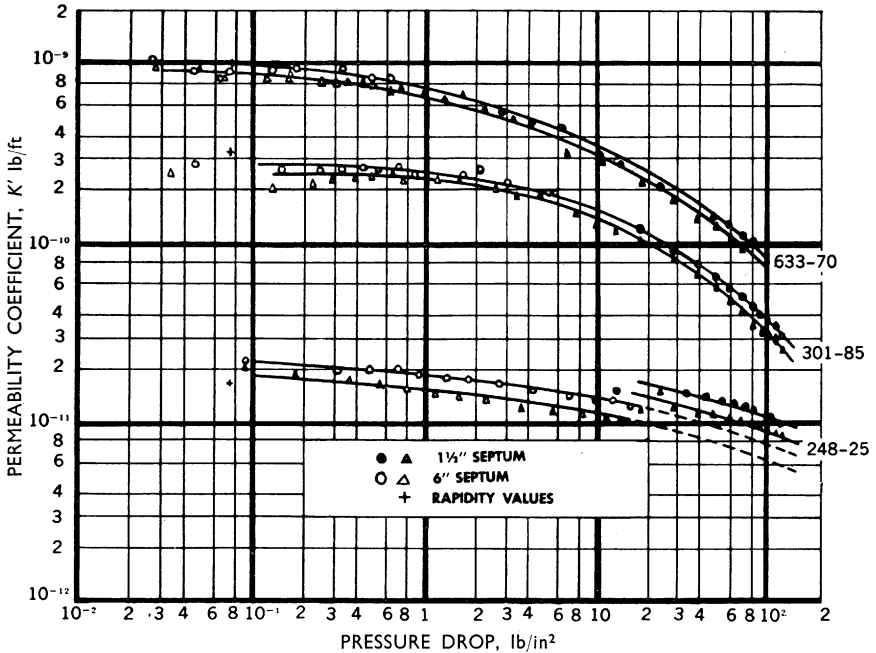


Fig. 3—Filter paper permeability as a function of pressure drop across the sheet (The Eaton-Dikeman Company)

time is halved; a further increase in the moisture content, however, hardly causes any further change. It would appear that the contact angle between the aqueous solution and the paper surface at first decreases until the pore walls are covered with a monomolecular layer of water, after which it remains fairly constant.

Arlov<sup>(37)</sup> has studied the penetration of paper by water in relation to sizing, density and surface roughness, using contact angle measurements. For unsized papers, the penetration rate increased with bulk and surface

roughness, the opposite being the case for sized papers. Evidently, this is due to the interdependence of roughness, contact angle and capillarity.

Back and Lundin,<sup>(38)</sup> too, have carried out measurements of the apparent contact angle between water and the paper surface and found that the contact angle, which is influenced by the roughness of the paper and the chemical nature of its surface (presence of hydrophobic rosin or aluminium resinate or of hydrophilic cellulose), represents a well-defined surface characteristic only so long as the water uptake is negligible while the measurements are being carried out.

### *Water vapour*

*Permeability*—For air and all the permanent gases, the permeability of paper can be calculated for any mean pressure by an air permeability test on the basis of simple laws. When water vapour permeates paper, however, the effect of surface diffusion is added, as already mentioned, resulting in a much higher permeability in comparison with air when the relative humidity (rh) is greater than an approximate figure of 25 per cent.

Vollmer has measured the permeability of two papers,\* which, as a result of different times of beating, differed considerably in density and mean pore radius. Permeability by both air and water vapour were plotted against rh (20°C) as shown in Fig. 4, from which it will be seen that at first the curves for permeation by air and water vapour respectively run parallel, but, as shown by the steepness of the curves, much more water vapour than air permeated the paper beyond 25 per cent rh. Surface diffusion of the water molecules adsorbed by the pore walls has raised the rate of flow.

The equation established by Vollmer for determining the additional transfer makes it possible to calculate permeability by water vapour as a function of rh from the air permeability, the adsorption isotherm and a calibration measurement. Schaschek<sup>(39)</sup> has carried on these studies and determined the dependence of surface diffusion on temperature.

### *Distribution of moisture and heat through the thickness during adsorption and desorption*

In recent studies, Pohl and Brecht<sup>(40)</sup> investigated the problem of the interrelationship between moisture changes and temperature changes in paper and the distribution of moisture and temperature during a process of equilibration.

\* Paper *a*: 61° S.R., 1.015 g/cm<sup>3</sup>, mean pore radius  $9.9 \times 10^{-5}$  cm  
 Paper *b*: 83° S.R., 1.092 g/cm<sup>3</sup>, mean pore radius  $7.7 \times 10^{-5}$  cm



These studies were based on equations given by Krischer<sup>(41)</sup> for the exchange of moisture and heat in hygroscopic materials. To allow mathematical evaluation, however, considerable simplifications had to be used on account of the complex nature of the porous structure of paper.

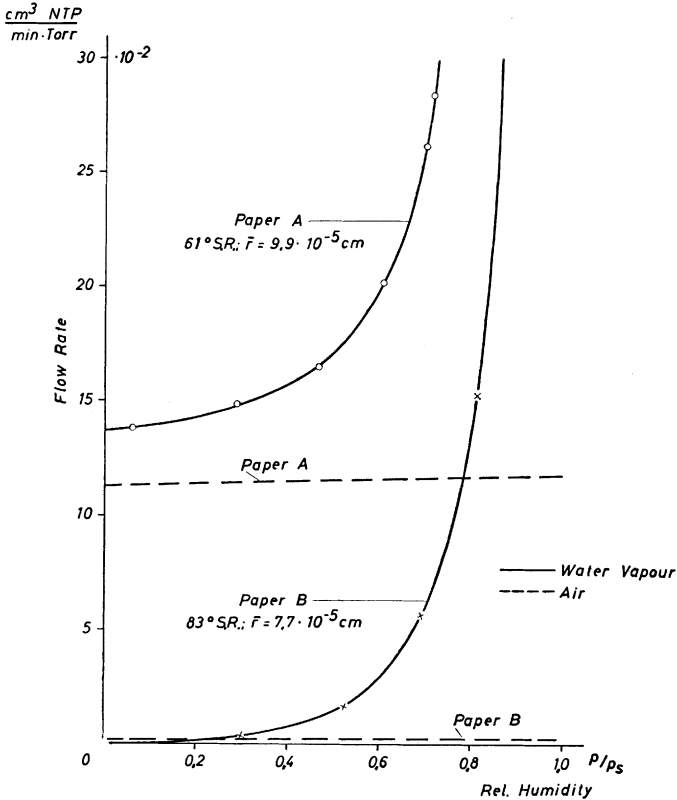


Fig. 4—Air permeability and water vapour permeability (Vollmer)

The differential equation for transfer of moisture is as follows—

$$\kappa \frac{\partial^2 F}{\partial z^2} - \frac{\partial F}{\partial t} + \frac{\delta'}{\mu} \frac{\partial^2 \gamma_D}{\partial z^2} - \psi \frac{\partial \gamma_D}{\partial t} = 0 \quad \dots \quad (13)$$

and for transfer of heat—

$$\lambda \frac{\partial^2 \theta}{\partial z^2} - c\tau \frac{\partial \theta}{\partial t} + r \left( \frac{\delta'}{\mu} \frac{\partial^2 \gamma_D}{\partial z^2} - \psi \frac{\partial \gamma_D}{\partial t} \right) + q_E = 0 \quad \dots \quad (14)$$

An explanation of the symbols used will be found in Table 2.

TABLE 2—LIST OF ABBREVIATIONS

	<i>Symbol</i>	<i>Units</i>
Weight per unit volume	$\tau$	kg/m <sup>3</sup>
Moisture content	$F$	kg/m <sup>3</sup>
Temperature	$\theta$	°C
Heat development in the material	$q_E$	kcal/m <sup>3</sup> h
Void volume	$\psi$	m <sup>3</sup> /m <sup>3</sup>
Specific heat	$c$	kcal/kg °C
Heat conductivity coefficient	$\lambda$	kcal/hm °C
Moisture conductivity coefficient	$\kappa$	m <sup>2</sup> /h
Specific gravity of water vapour	$\gamma_D$	kg/m <sup>3</sup>
Effective diffusion coefficient for water vapour in air	$\delta'$	m <sup>2</sup> /h
Heat of evaporating of water including heat of sorption	$r$	kcal/kg
Diffusion resistance coefficient of material	$\mu$	

For only small changes in moisture content and temperature, the adsorption isotherm can be plotted linearly, two differential equations coupled with each other being thus obtainable from equations (13) and (14). These can be solved analytically for edge conditions of the first kind\* according to the method of Henry.<sup>(42)</sup> Pohl and Brecht proceeded according to the graphical method given by Krischer,<sup>(43)</sup> which also permitted solutions for edge conditions of other types.†

Results of the above-mentioned calculation are shown in an example of two tracing papers that differ only in thickness. Fig. 5 and 6 show the way in which the moisture content and the temperature of the paper alter when the paper is exposed to a change of humidity from 85 per cent to 45 per cent r.h.

Moisture distribution is shown at the bottom, the corresponding temperature distribution above. Not only does the thinner paper attain equilibrium considerably faster than the thicker paper—45 sec compared with 121 sec—but it also has the smaller moisture gradient at every instant. The temperature in the sheet dropped very quickly by about 0.1°C, then rose slowly again to the original value. The minimum temperature is the same for thick and thin papers, whereas the times needed for changes in temperature correspond to the respective moisture changes.

For the change in moisture content, the decrease was at first quite marked—mainly at the two surfaces—as indicated on the extreme right and left of the diagram. Subsequently, it slowed down, becoming more marked in the interior of the sheet, until after a certain time the now reduced moisture content was equally distributed over the cross-section.

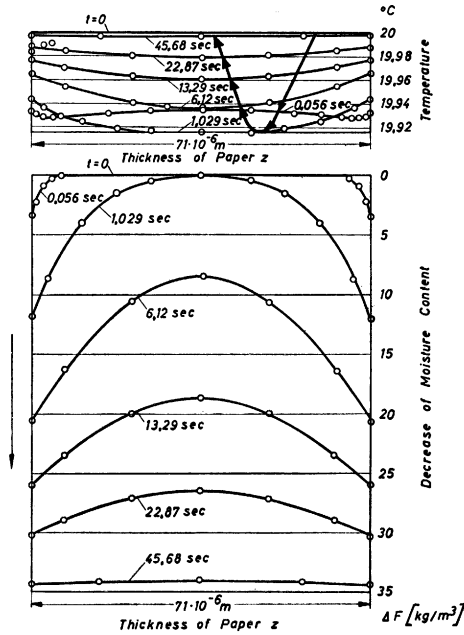
\* Edge conditions of the first kind: heat transfer coefficient  $\alpha = \infty$  and moisture transfer coefficient  $\beta = \infty$

† Edge conditions of other types:  $\alpha, \beta$  equal definite functions

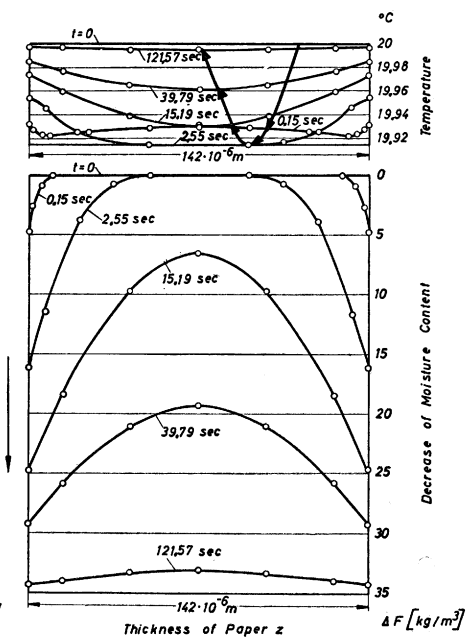
*Influence of water vapour and water on physical properties*

The changes in the properties of paper, produced by exchange of moisture with the surrounding air or by water, are of great practical importance.

With increasing moisture content, paper becomes softer and more plastic; build-up of static electricity and the tendency to fluffing are reduced and the paper tends to lie flatter; on the other hand, the smoothness of



**Fig. 5**—Distribution of temperature and moisture content in paper  
(85 to 45 per cent rh;  $\mu=100$ ;  
 $z=71 \times 10^{-6}$  m)  
(Pohl and Brecht)



**Fig. 6**—Distribution of temperature and moisture content in paper  
(85 to 45 per cent rh;  $\mu=100$ ;  
 $z=142 \times 10^{-6}$  m)  
(Pohl and Brecht)

calendered papers may suffer, especially in papers containing groundwood. Moisture exchange also has an important influence on dimensional stability and curl.

To demonstrate the dependence of strength on moisture content,<sup>(44)</sup> the strength curves for a paper made from sulphite woodpulp are shown in Fig. 7. On the left are the properties statically tested, on the right those

dynamically tested, both plotted against moisture content. The maximum value for all properties is not achieved in completely dry paper, but is obtained when the moisture content is fairly high. This is not so marked for the statically determined stretch, folding, tearing and edge tear resistances. The moisture content also determines the difference between machine-direction and cross-direction values for each of these properties, since this difference is always greatest at optimum moisture level.

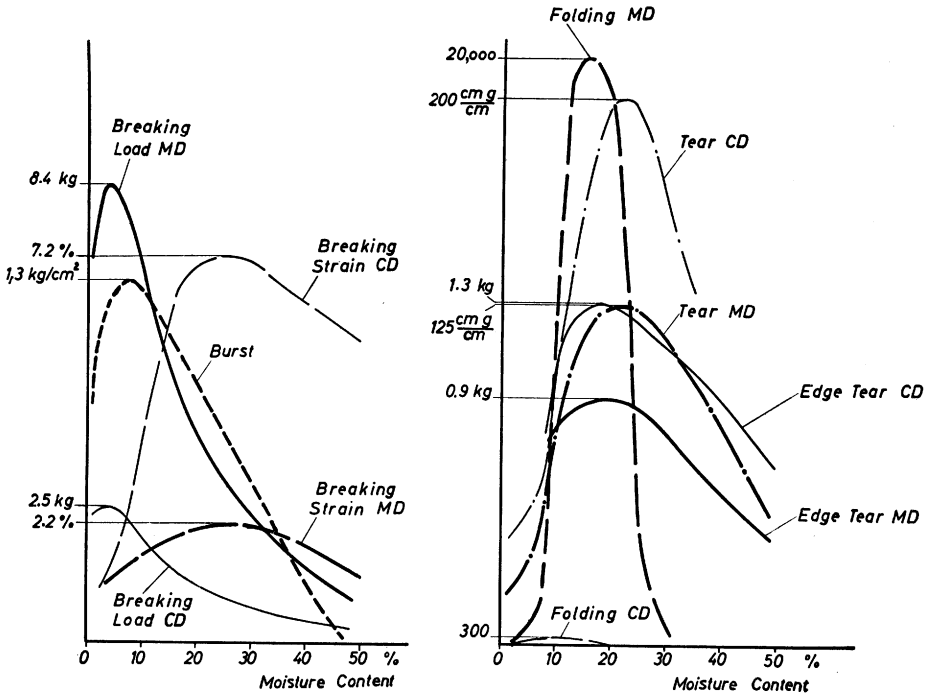


Fig. 7—Moisture content and strength properties of a paper (Brecht)  
(sulphite paper 43 g/m<sup>2</sup>)

Something should also be said about the results of recent investigations that have widened our knowledge of dimensional instability and curl—each one depending to a marked degree on changes in humidity.

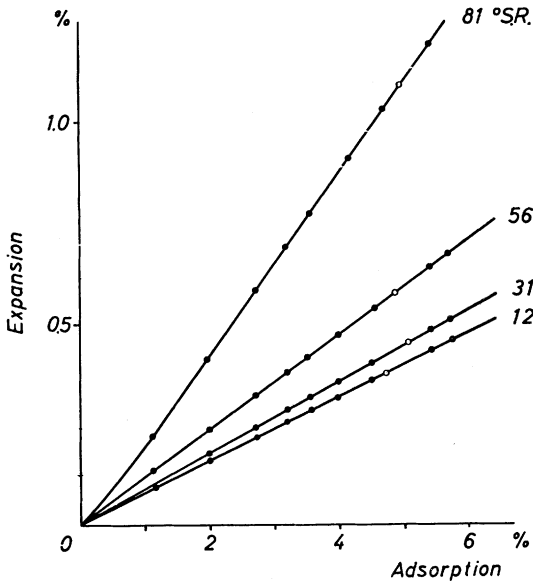
#### *Dimensional instability*<sup>(45)</sup>

#### *Beating*

Rance<sup>(46)</sup> has pointed out that the change in the length of a sheet of paper is directly proportional to the change in its moisture content. Neverthe-

less, this proportion depends on a number of variables. As shown in Fig. 8, a change in moisture content in a highly beaten pulp results in a much greater change in length than in a freely beaten pulp. This behaviour can be explained satisfactorily by Rance's theory of interfibre and fibre shrinkage.

The remarkable effect of beating is shown also in the time required for dimensional changes to take place. Fig. 9 (from Brecht and Hildenbrand) shows at the top the expansion of a softwood sulphite pulp beaten to different



**Fig. 8**—Influence of beating on the relationship between moisture adsorption and moist expansion from 65 to 90 per cent rh (Brecht and Hildenbrand)

(bleached soft spruce sulphite pulp)

degrees of wetness during conditioning, showing how air of 90 per cent rh, with a flow rate of about 20 m/min, influences paper first conditioned at 65 per cent rh.

In Fig. 9 (bottom), the half-value time method of assessment was used as a measure of the rate of expansion (period that has elapsed when half of the final value is obtained). It increased with beating, since the resistance to penetration increased with increasing sheet density. As will be seen, humidity increased from 65 to 90 per cent.

### Dimensional instability and energy for rupture

In Fig. 10, the dotted line on the extreme left shows the soft sulphite pulp; the dotted line next to it the soft sulphate pulp; then follow the semi-chemical pulp and the strawpulp on the right (solid lines), the hard sulphate pulp (heavy line) and the hard sulphite pulp (thin line). At almost uniform expansion, the tensile strength increases in that order. This is attributed to the fact that increased beating of soft pulps produces hardly any increase in

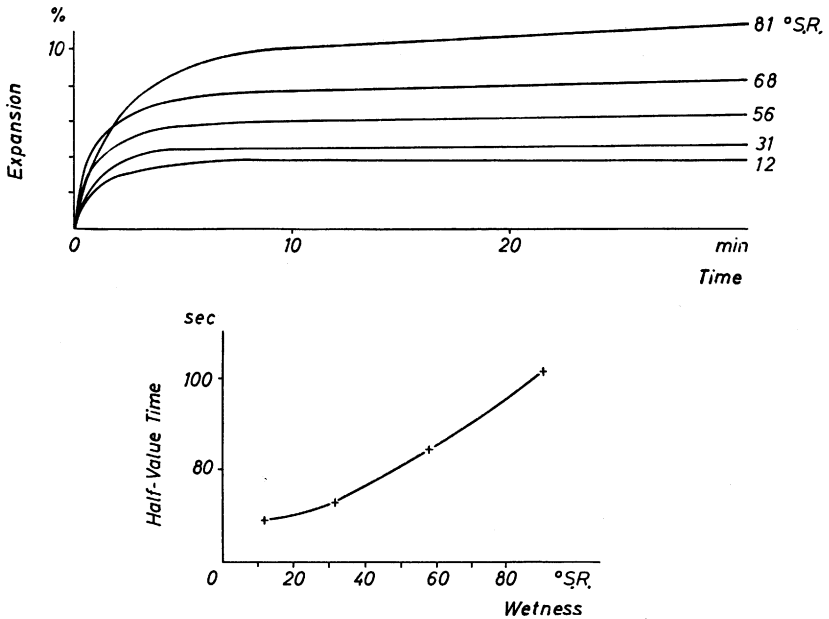


Fig. 9—Influence of beating on the development of moist expansion from 65 to 90 per cent rh (Brecht and Hildenbrand)  
(bleached spruce sulphite pulp)

strength, whereas dimensional stability decreases still further. This may be expressed differently by saying that hard pulps require less beating to achieve a given strength level; therefore, they expand less under the influence of moisture at that level.

### Fibre orientation

Fibre orientation is of great importance for dimensional stability and this is shown in Fig. 11. The anisotropic sheet differs from the isotropic

(in which the fibres are distributed at random in all directions) by showing only little reaction in the machine-direction, but an extremely marked one in the cross-direction—which is in this instance the main direction in which the fibres themselves swell.

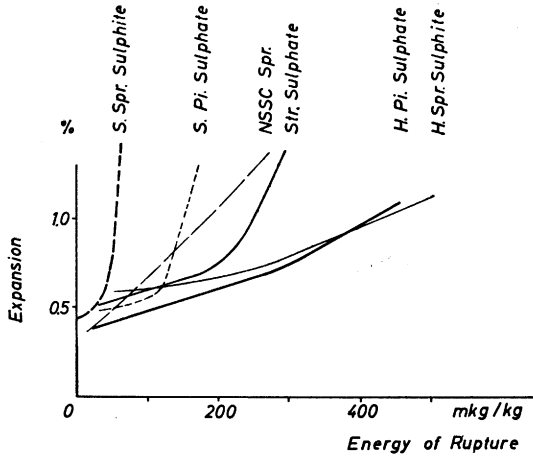


Fig. 10—Moist expansion and energy of rupture (Brecht and Hildenbrand)

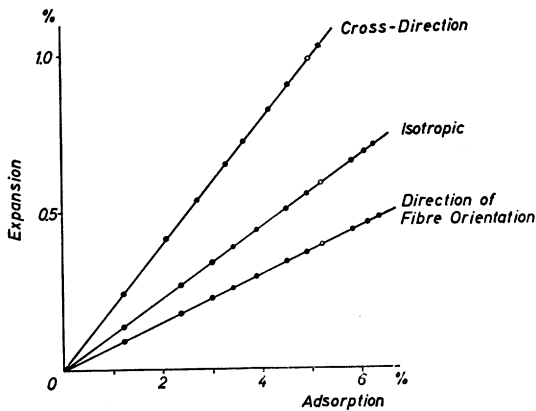


Fig. 11—Influence of fibre orientation on the relation between moisture adsorption and moist expansion (Brecht and Hildenbrand) (bleached soft sulphite pulp, 53 °S.R.)

Tension during the drying of paper

Fig. 12 (top) shows that a change in the moisture content of the finished paper causes least dimensional change in the direction of the sheet in which drying tension was highest. If tension is high, the graphs are curved, since

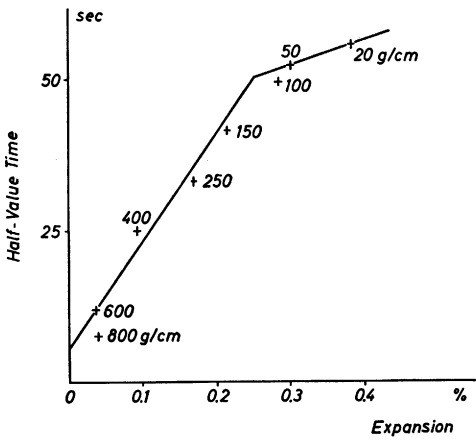
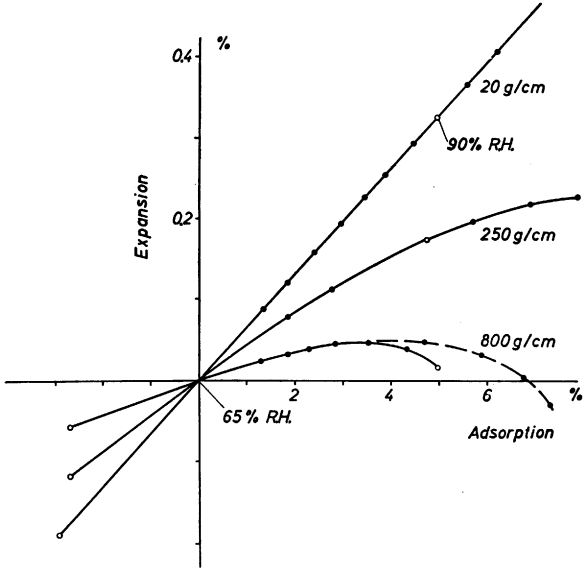


Fig. 12—Influence of drying tensions on moisture adsorption, moist expansion and half-value time (Brecht and Hildenbrand)



with increasing adsorption the dried-in strains are released and cause shrinkage. This is clearly seen in the graphs of the high (800 g/cm) tension. Here, a difference can be observed between conditioning from 65 per cent to 90 per cent rh (continuous line) and from 65 per cent to about 100 per cent rh (dotted line). The dried-in strains cause contraction, which is superimposed on the expansion; so the release of these strains is a process dependent on time. Therefore, in these graphs, the points of equal adsorption do not correspond to equal periods.

Fig. 12 (bottom) shows that, in the zone of higher moisture content (conditioned from 65 per cent to 90 per cent rh), the half-value time increases with decreasing drying tension—that is, with increasing expansion. The half-value time is therefore always smaller in the direction of the tension compared with the cross-direction value. This is at first difficult to understand, as both expansions are due to the same process. Here, the two processes already mentioned—that of expansion and the release of the dried-in strains—are superimposed. In consequence of this, the exchange seems to take place more rapidly and the half-value time becomes shorter as the dried-in strains become greater.

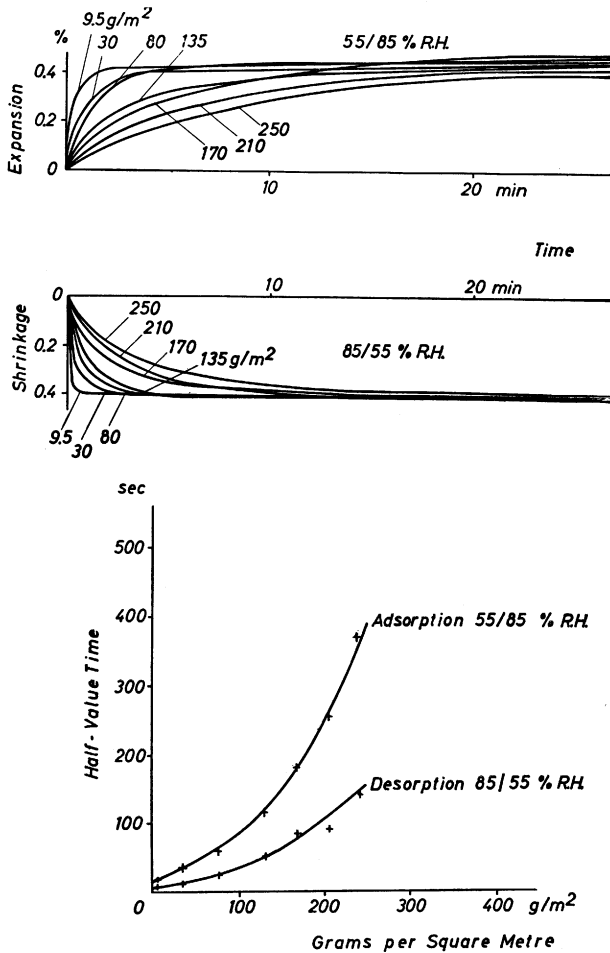
#### *Basis weight and density*

The influence of basis weight is shown in Fig. 13. The graphs at the top show that the same final state of expansion or shrinkage is always obtained if conditioning is sufficiently prolonged. Below, it is shown that the half-value time required for adsorption and desorption is prolonged when basis weight is high. Likewise, it can be seen that adsorption takes longer than desorption when the moisture content is relatively high initially (corresponding to 65 per cent rh), because the amount of moisture exchanged is higher in the former case.

Furthermore, papers of higher porosity, but of equal basis weight, do not require as much time to expand as do dense papers; hence, it does not matter whether the higher density is obtained by beating or by calendering.

#### *Flow rate of conditioning air*

Fig. 14 shows that, compared with stationary air, even a very low rate of flow accelerates expansion. An increase beyond 10 m/sec, however, has little effect. Most of all, it is clear how much longer it takes to achieve moisture equilibrium, if, at a relatively small difference in vapour pressure (65 per cent to 90 per cent rh), paper has to adsorb more moisture than at the relatively steep vapour pressure gradient corresponding to an increase from 25 per cent to 65 per cent rh.



**Fig. 13**—Basis weight and development of moist expansion  
(Brecht and Hildenbrand)  
(bleached spruce sulphite pulp)

### *Curl*

Curl is a deviation from the plane, defined by its extent and its direction. It may be caused by mechanical conditions: for example, if the paper is bent round an edge or held down on a curved surface. In this way, relaxation causes structural changes in the stretched outer layers.

The other cause—the only one of interest in the present case—is the relationship between changes of moisture and variations in the dimensions of paper. This can be classified in the following ways—

- (a) Moisture applied to one side of the paper only.
- (b) Moisture applied equally and simultaneously to both sides of paper not uniform in its structure or moisture content throughout its thickness.

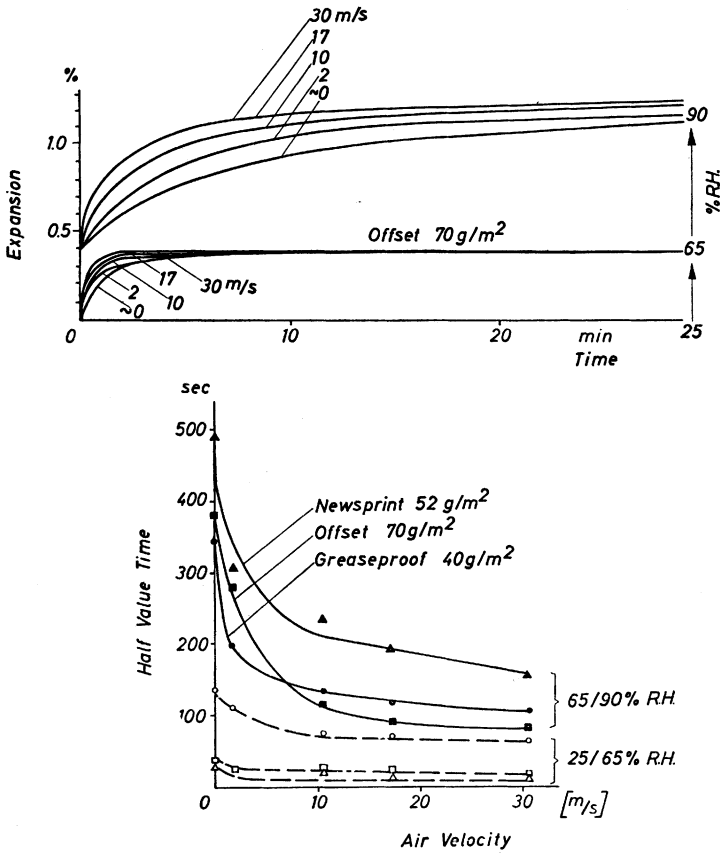
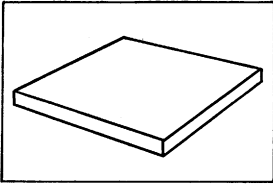


Fig. 14—Velocity of air and development of moist expansion (Brecht and Hildenbrand)

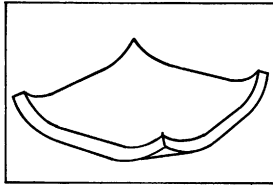
*Change of humidity on one surface of the paper (47)*

Fig. 15, taken from a study of changes in atmospheric humidity on one side of the paper and its effect on curl, illustrates schematically how and when this curl takes place.

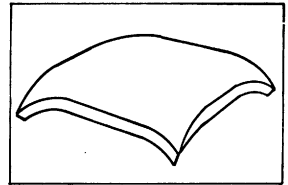
**Isotropic**



**A**  
*Initial Condition*

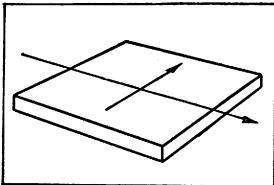


**B**  
*Moistening from below  
or/and  
Drying from above*

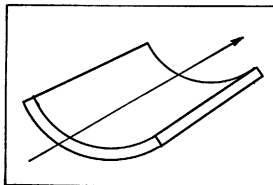


**C**  
*Moistening from above  
or/and  
Drying from below*

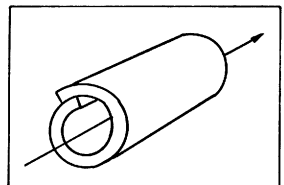
**Anisotropic**



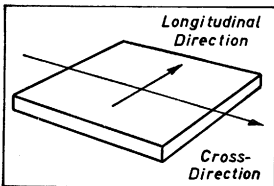
**D**  
*Initial Condition*



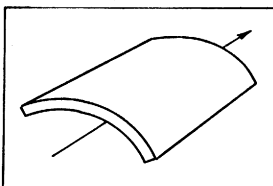
**E**  
*Moistening from below  
or/and Drying from above*



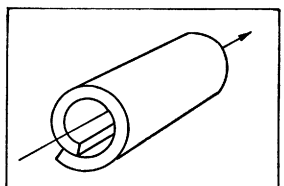
**F**



**G**  
*Initial Condition*



**H**  
*Moistening from above  
or/and Drying from below*



**I**

**Fig. 15**—Curl caused by moisture exchange on one side of the material  
(Brecht, Räderer and Weitzel)

If a porous and isotropic plate *A*, with uniform dimensional stability throughout its thickness, is subjected on one side to moist or dry air, this side will either expand or shrink. Fig. *B* and *C* show how the edges curl. If the material is anisotropic, for which the arrows of different lengths indicate non-uniform moist expansion, the surface exposed to the humid conditions expands preferentially in the direction of greater moist expansion. Owing to the dimensional stability of the opposite surface not affected by moisture exchange, the sheet curls and may form a tube in extreme cases. The axis of curl is parallel to the direction of smaller moist expansion.

This type of curl is intensified by the moisture gradient existing between the two surfaces of the paper and is accelerated by the increased air flow causing moisture exchange.

Of all the properties, moist expansion is the one mainly responsible for this kind of curl. As already shown, the expansion is greatly increased by beating. Moreover, curl increases with the anisotropy caused by the fibre orientation and is greater for a dense paper with high resistance to permeation than for a porous paper. On the other hand, basis weight is of importance more for the speed with which the final condition is attained than for its extent. If basis weight is low, the stiffness of the sheet (which may counteract curl) is much less than in a heavier sheet. Hence, thick paper curls more slowly than thin paper.

In practice, this system operates in all cases in which changes in atmospheric conditions occur on one side of the outermost sheet of a roll or stack of paper, whilst the other side is unaffected or not affected to the same extent.

#### *Equal changes of humidity on both sides of the paper*

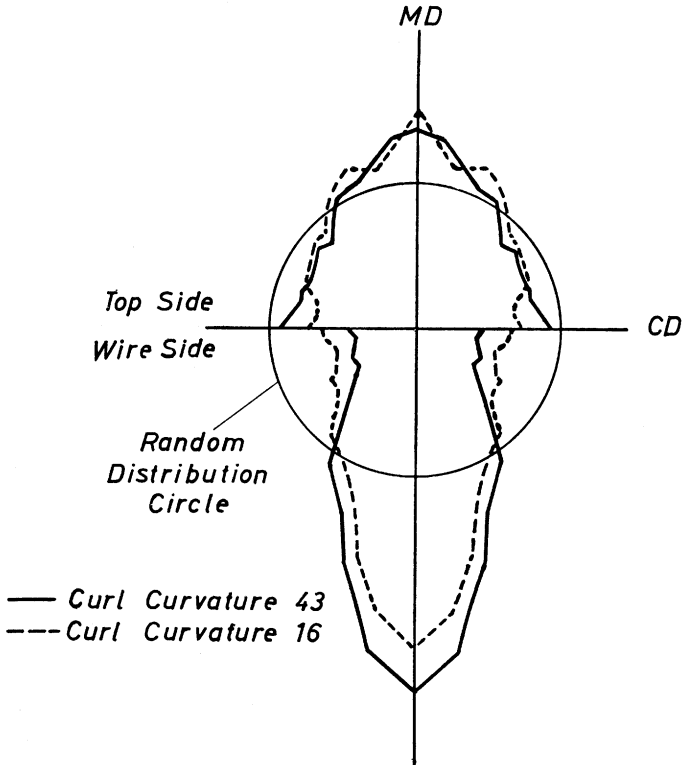
If a similar change of humidity takes place simultaneously on both sides of a sheet (for instance, when it is exposed to different atmospheric conditions), such a sheet will curl only when the structure is not uniform throughout its thickness.

Credit is due to Gallay<sup>(48)</sup> and his co-workers for having fundamentally investigated these relationships. Their findings are briefly summarised in the following paragraphs.

The primary cause of curl is the non-uniform fibre orientation through the thickness of a sheet. While the fibres on the wire side are preferentially oriented in the machine-direction, the orientation in the upper layers is less pronounced. A change in humidity is accompanied by a change in fibre volume, which, as is known, affects the thickness of the fibre ten to twenty times as much as its length. It causes, therefore, more marked dimensional

changes in cross-direction on the wire side, where fibre orientation is greater than on the top side. The sheet therefore not only expands, but it also curls.

Fig. 16 shows the fibre orientation for the wire and the top sides of two sheets of paper: paper 1, with the greater difference in orientation between the two sides, curled  $2\frac{1}{2}$  times as much as paper 2.\*



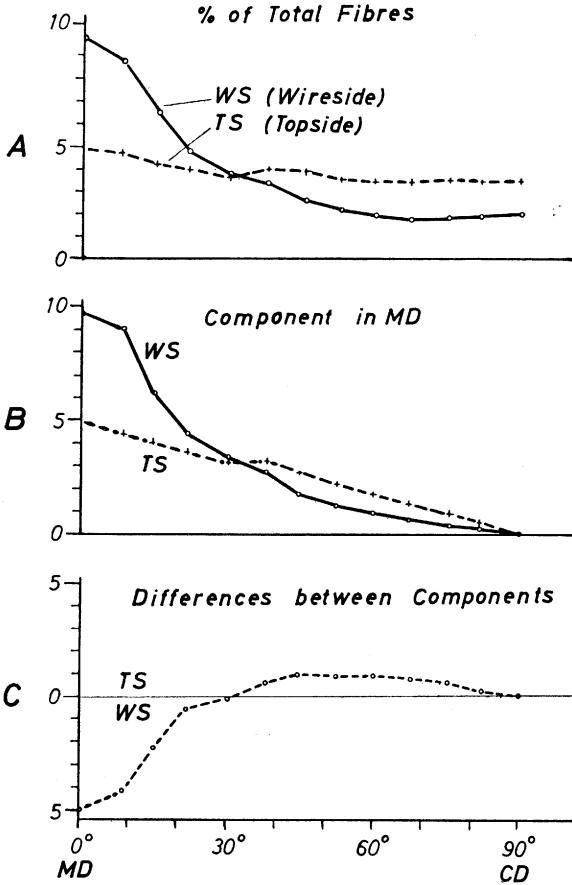
**Fig. 16**—Fibre orientation distribution on top and wire sides of paper (Gallay and co-workers)

Fig. 17 shows the fibre orientation for the wire and top sides of a sheet at various angles between machine-direction and cross-direction, the components of the number of fibres in the machine-direction and the difference in these components between top and wire side. On the wire side, fibre orientation in the machine-direction is very marked up to angles of  $30^\circ$ .

\* Measurement of degree of curl according to Gallay—Paper samples  $3 \text{ in} \times 3 \text{ in}$  are dried by an infra-red lamp to constant dryness and the resulting curvature ( $=1/\text{radius}$ ) is used as measuring value.

At greater angles, there is a slight preference for orientation in the machine-direction on the top side.

Many papers were tested and curl was plotted against the difference in



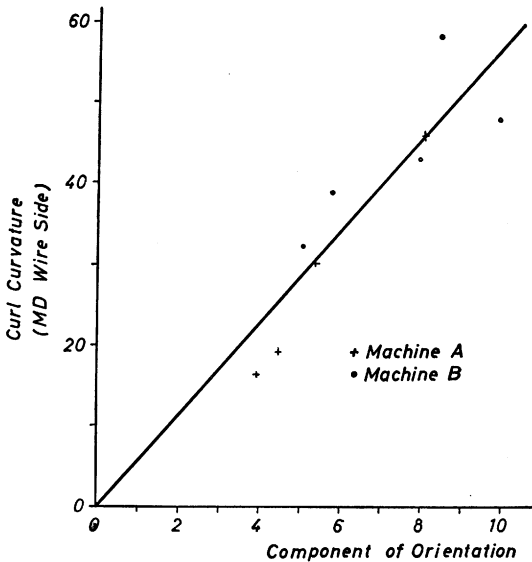
**Fig. 17**—A Percentage of total fibres at various angles to machine-direction

**B** Components of number of fibres in machine-direction (no. of fibres  $\times$  cosine of angle) at various angles to machine-direction

**C** Differences between top side and wire side components at various angles to machine-direction (Gallay and co-workers)

fibre orientation between wire and top sides. The resulting straight line of Fig. 18 proves that, in fact, paper curl is proportional to this difference in fibre orientation.

On drying, all these papers curled, as expected, concavely towards the wire side and with the axis of curl in the machine-direction. Besides, papers also exist in which the axis of curl is oriented at an angle to the machine-



**Fig. 18**—Relationship between curl curvature and component of orientation (Gallay and co-workers)

direction. This phenomenon may be caused by angular orientation on coming out of the slice or by an oblique draw.

### **Conclusion**

It is obvious that a comprehensive picture of the influence exercised by the structure of paper on its behaviour when exposed to liquid media cannot be attained without a thorough knowledge of all the characteristics and details of paper structure. Really reliable data are, however, not as yet available. The known laws governing penetration and permeation through tubes and capillaries give only approximate results, so also do those that refer to porous



systems. This difficulty is especially noticeable when swelling effects linked with structural changes of paper are concerned. Furthermore, it appears desirable to find better methods for measuring the penetration of liquids into papers of various kinds. In the technological field, however, much useful knowledge has already been gained.

## REFERENCES

1. Kozeny, J., *Sitzber. Akad. Wiss. Wien, Math. Naturw.*, 1927, Klasse 136 (Abt. 11a), 271
2. Carman, P. C., *Trans. Inst. Chem. Eng. (London)*, 1937, **15**, 150–166
3. Langmuir, I. and Taylor, J. B., *Phys. Rev.*, 1932, **40** (2), 463–464
4. Volmer, M., *Trans. Faraday Soc.*, 1932, **28**, 359–363
5. Brunauer, S., Emmett, P. H. and Teller, E., *J. Amer. Chem. Soc.*, 1938, **60** (2), 309–319
6. Korn, R. and Burgstaller, F., *Handbuch der Werkstoffprüfung* (Springer, Berlin, 1953), vol. 4
7. Baird, P. K. and Hrubesky, C. E., *Tech. Assoc. Papers*, 1930, **13** (1), 274–277; *Paper Trade J.*, 1930, **91** (4), 48–51
8. Carson, F. T., *J. Res. Nat. Bur. Stand.*, 1940, **24** (4), 435–442
9. Simmonds, F. A., *Paper Trade J.*, 1933, **97** (10), 40–42
10. Foote, J. E., *Paper Trade J.*, 1939, **109** (14), 40–48
11. Vollmer, W., *Chem. Ing. Tech.*, 1954, **26** (2), 90–94
12. Tollenaar, D., *Chem. Weekblad*, 1948, **44**, 753–757
13. Tollenaar, D., *Appl. Sci. Res.*, 1954, **A4**, 453–456
14. Corte, H., *Fundamentals of Papermaking Fibres*, Ed. F. Bolam (Technical Section, B.P. & B.M.A., Kenley, 1958), 301–331
15. McKnight, T. S., Marchessault, R. H. and Mason, S. G., *Pulp & Paper Mag. Can.*, 1958, **59** (2), 81–88
16. Wakeham, H., *Textile Res. J.*, 1949, **19** (10), 595–605
17. Ritter, H. L. and Drake, L. C., *Ind. Eng. Chem. Anal.*, 1945, **17** (12), 782–786
18. Carson, F. T., *Paper Trade J.*, 1934, **99** (11), 25–34
19. Manegold, E., *Kolloid-Z.*, 1937, **81** (3), 269–294
20. Publitz, W. J., Dappen, J. W., Wayne, J. and Van den Akker, J. A., *Tech. Assoc. Papers*, 1948, **31**, 305–315
21. Lane, W. H., *Paper Trade J.*, 1943, **117** (3), 26–27
22. Doughty, R. H., Seborg, C. O. and Baird, P. K., *Paper Trade J.*, 1932, **94** (24), 31–33
23. Doughty, R. H., *Paper Trade J.*, 1932, **95** (10), 31–38
24. Stoewer, W., *Wochbl. Papierfabr.*, 1933, **64** (4), 57–59
25. Tollenaar, A., *Textil-Rund.*, 1957, **12** (2), 81–84
26. Gillespie, T., *J. Colloid Sci.*, 1958, **13** (1), 32–50
27. Gillespie, T., *J. Colloid Sci.*, 1959, **14** (2), 123–130
28. Olsson, I., Pihl, L., *Svensk Papperstidn.*, 1952, **55** (7), 233–237
29. Olsson, I., Pihl, L., *Intern. Bull. for Printing & Allied Trades*, 1954, (67), 19–24
30. Carlsson, G. E., *Allg. Papier-Rund.*, 1954, (12), 625–627; (13), 670–674; (14), 714–715
31. Laroque, G. L., *Pulp & Paper Mag. Can.*, 1937, **38** (2), 77–84
32. Smith, A. H. and Coupe, R. R., *Intern. Bull. Printing & Allied Trades*, 1952, (61), 21–25
33. Coupe, R. R. and Smith, A. H., *J. Oil & Colour Chem. Assoc.*, 1956, **39**, 579–604
34. The Eaton Dikeman Co., Filbertown, *Handbook of Filtration*, 1960
35. Seiler, C. J., *Tappi*, 1957, **40** (10), 201A–203A
36. Arledter, H. F., *Tappi*, 1957, **40** (7), 513–519
37. Arlov, A. P., *Norsk Skogind.*, 1951, **5** (12), 403–408
38. Back, E. and Lundin, B., *Svensk Papperstidn.*, 1955, **58** (20), 758–763

39. Schaschek, H., *Chem. Ing. Tech.*, 1956, **28** (11), 698–702
40. Pohl, A., *Dissertation*, 1961, Tech. Hochsch., Darmstadt
41. Krischer, O., *Die wissenschaft. Grundlagen d. Trocknungstechn.* (Springer, Berlin, 1956)
42. Henry, P. S. H., *Proc. Roy. Soc. A*, 1939, **171**, 215–241
43. Krischer, O., *VDI-Forsch. Heft.*, **415**, 1942, 1–22
44. Brecht, W., *Das Papier*, 1947, **1** (7/8), 145–151
45. Brecht, W. and Hildenbrand, W., *Das Papier*, 1960, **14** (10a), 610–624
46. Rance, H. F., *Tappi*, 1954, **37** (12), 640–654
47. Brecht, W., Räderer, P. and Weitzel, W., *Das Papier*, 1959, **13** (11/12), 237–244
48. Glynn, P., Jones, H. W. H. and Gallay, W., *Pulp & Paper Mag. Can.*, 1959, **60** (10), T 316–T 323

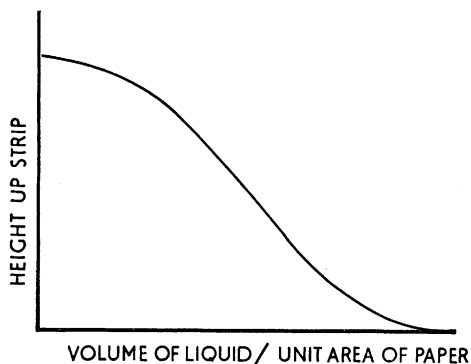
## Transcription of Discussion

### DISCUSSION

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MR. R. R. COUPE: My first point concerning the penetration of non-interacting liquids is that there is a fundamental difference between the flow of liquid into a single capillary tube and that into a porous structure like paper. As liquid rises, the whole of the tube below the meniscus is filled; but with paper there are always air spaces below the height to which some liquid has risen. It can be shown experimentally that the liquid held on the strip is distributed in the way shown in Fig. D12.

In practice, most interest centres round the penetration in a direction at rightangles to the plane of the sheet, but the same considerations must apply. The shape of the penetration function would be similar and the kinetics can



*Fig. D12*

probably be formulated in a similar way, with the introduction of appropriate shape factors.

My second point concerns the fact that, when liquid is penetrating paper under practical conditions, there is no large reservoir of liquid. In fact, the amount of liquid available may be small in relation to the pore volume of the sheet and this has a very significant effect on the fundamentals of penetration. The depth to which liquid penetrates under a given pressure (200–1 000 lb/in<sup>2</sup> range) and time (several centiseconds) is related to the thickness of liquid film available (range up to 25 microns) by a function shown in Fig. D13.

The actual curve depends upon the structure of the sheet in question—for example, a maximum penetration is not reached at any thickness up to

25 microns (maximum experimental limit) with an open-structured antique paper.

Using the techniques developed at PATRA,<sup>1</sup> it has been possible to study the dependence of distance of penetration on the variables of pressure, time and viscosity. The relationship found experimentally is—

$$h = C \left( \frac{pt}{\eta} \right)^{1/2}$$

where  $c$  is a constant.

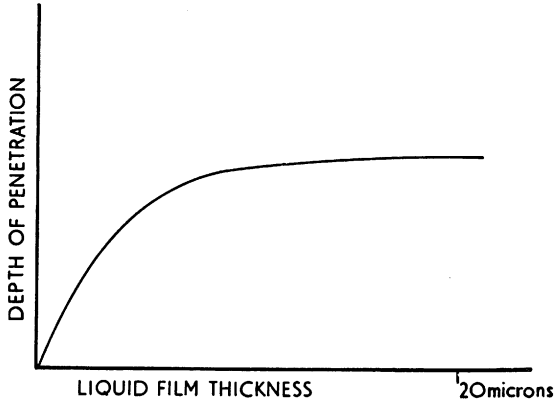


Fig. D13

This is the same form of expression that can be derived by integration from the Darcy equation—

$$\frac{dl}{dt} = K \frac{P}{\eta l}$$

This agreement with classical theory is very satisfactory, until one remembers that Darcy's law was derived and has been verified from the flow of liquids through compacted beds of incompressible substances like sand, cement and pigments.

I am not suggesting that these results show that paper is an incompressible network, for clearly it is not, but that they are throwing some interesting light on the influence of structure and compressibility on fluid flow.

<sup>1</sup> Coupe, R. R. and Hsu, Baysung, *Appl. Sci. Res.* (Section A), 1961, **10** (3-4), 253-264

## Discussion

DR. E. BACK: In respect to the water resistance of sized papers, there are important limitations in the equations (10), (11) and (12) because of the contact angle. According to electron microscope work, the aluminium soaps formed in paper sizing appear as discrete hydrophobic particles on the hydrophilic cellulose. The approach of Phillippoff<sup>2</sup> to the mean contact angle of heterogeneous surfaces must be considered.

For the effect of surface roughness on contact angles, I would like to draw attention to fundamental measurements of Bartell and Shephard.<sup>3</sup>

Actually, we measure an apparent static contact angle of water as high as 120°–130° on sized papers. In spite of this, the water penetrates.

In dimensional stability, the two main independent parameters are the equilibrium dimensional range (EDR) and the permanent dimensional change (PDC), obtained separately after cycling the paper repeatedly between two predetermined relative humidities.\* In wet expansion, both these parameters are involved. The PDC is mainly dependent on drying stresses in the paper; the EDR is mainly determined by the fibre and stock properties. With a given papermaking stock, the only efficient way to reduce the EDR is to transform hydrogen bonds into covalent bonds, for example by heat treatment in the presence of a catalyst. This can be done to some extent and, because this bond transformation (dehydration) in heat treatment takes place in a fairly water-free state, the paper compared to a given relative humidity has shrunk. Thus, the PDC of this paper is low or even negligible.

MR. J. MARDON: I wish to present a written contribution from Prof. Scheidegger on flow through porous media. The subject matter of his contribution is quite important to us all in the paper industry. We tend to accept uncritically the Kozeny-Carman equation, which is almost completely suspect in the way we very often use it: in fact, it is numerically reliable only within a factor of ten.

DR. H. CORTE: I would like to stress the conceptual difficulties in defining geometrically what could be called a *pore* in a three-dimensional network of fibres. Such a definition not existing, we find the only way out is in a physical definition. This means that it depends on the experiment what a pore is.

MR. J. F. T. HARRIS: From the paper by Baird and Trubesky<sup>(7)</sup> are quoted figures for the apparent density and void volumes for normal papers. I wish to extend these figures to include filter paper.

<sup>2</sup> Phillippoff, W., Cooke, S. K. and Cadwell, D. E., *Mining Eng.*, 1952, 4 (3), 283–286

<sup>3</sup> Bartell, F. E. and Shephard, J. W., *J. Phys. Chem.*, 1953, 57 (2), 211–215; (4), 455–458

\* This has been pointed out by Hudson, Rance *et al.*

There are a number of commercially produced filter papers with apparent densities as low as 0.14 and with void volumes of over 90 per cent. In this type of paper, the proportion of the voids that exist as real pores is 90–95 per cent of the total void volume. This contrasts with the proportion of 1–2 per cent found by Baird in other types of paper.

DR. R. P. WHITNEY: I should like to point out that the Kozeny-Carman relation is still being applied extensively to flow through porous fibrous media such as paper, because it is still the best relation available. If the equation is used properly, with due regard to its limitation—for example, proper evaluation of the so-called Kozeny constant, which is not a constant at all—it will yield results far more reliable than the tenfold that Scheidegger mentions.

THE CHAIRMAN: I remember that, when I first started research work on permeability, the literature was full of criticisms of the Kozeny equation. The criticisms are just the same, but the equations are being used as effectively today as then. Kozeny's constant  $k$  is an empirical coefficient and people should really be careful how they use it.

MR. P. E. WRIST: Scheidegger's justifiable criticism of the Kozeny-Carman concept has given rise to the impression that, until such time as someone works out a statistical theory to replace it, we are left with nothing reliable to use in its place. I think that is not quite true. In fact, without many people realising it, Davies and Ingmanson have put forward an adequate empirical relationship in its place. The Kozeny-Carman concept is based on a capillary model, one in which the media is treated as a system of capillaries.

It was a concept put forward to relate the constant of proportionality in the Darcy equation to the porosity of the media and contains a 'constant' of its own that was to be independent of porosity. Within a narrow range of porosities, this is in fact almost true, hence the limited successes of the concept. At high porosities, however, the Kozeny-Carman 'constant' becomes a function of porosity, hence the criticism. More recently, Davies, working with gaseous flow through textile fibre beds and Ingmanson, working with water flow through beds of synthetic fibres of papermaking dimensions, have derived very similar empirical relationships correlating the Darcy constant with the mat porosity. A recent theoretical study of flow through parallel arrays of cylinders by Happel lends theoretical support to the Davies-Ingmanson equations. Fig. D14, taken from a forthcoming paper by Meyer,<sup>4</sup> shows that

<sup>4</sup> Meyer, H., *Tappi*, 1962, 45 (4), 296-310

Discussion

the theoretical curves of Happel for the dimensionless Darcy constant for flow perpendicular to and parallel to cylindrical arrays envelope the Davies-Ingmanson curves. At high porosities, the empirical curves fall midway between the two, as might be expected from a random array of the fibres. As the porosity decreases, the curves approach the curve for flow across the cylindrical array.

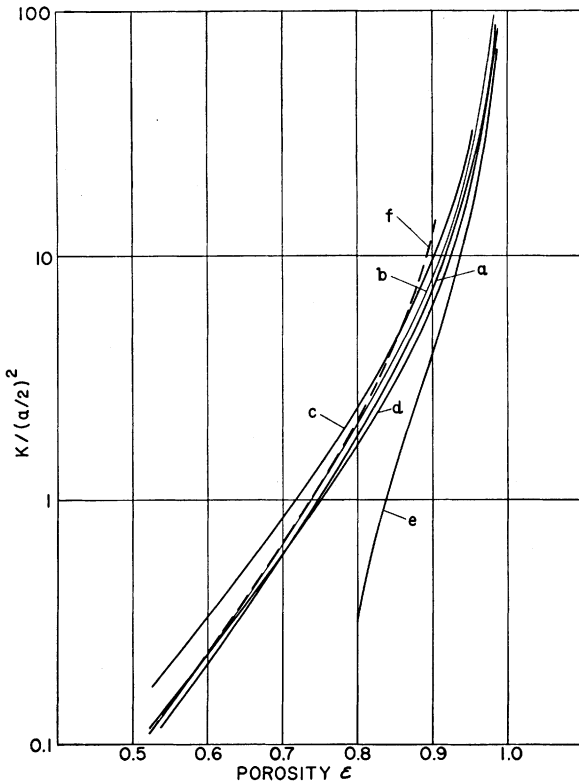


Fig. D14—Darcy constant as function of porosity  $\epsilon$

- Curve a: after Davies: equation (4.2)
- Curve b: after Ingmanson: equation (4.2)
- Curve c: after Happel: parallel, equation (4.3)
- Curve d: after Happel: perpendicular, equation (4.4)
- Curve e: after Hasimoto: perpendicular, equation (4.5)
- Curve f: after Kozeny-Carman: equation (4.1)

(From *Tappi*, 1962, 45 (4), 300)

## *Paper structure and fluids*

I suggest that, until such time that a more rigorous treatment is available, the empirical equation of Davies-Ingmanson, which is not based on a model at all, but in fact approximates results based on a 'fluid drag passed cylinders model', is a very satisfactory basis for a study of flow of fluids through fibrous mats such as paper. The appropriate references are contained in my paper to be presented on Friday.

PROF. W. BRECHT: This discussion shows that the subject dealt with presents complicated problems. One of them is the question whether the equation established by Kozeny and Carman can be applied to determine the permeability of fibrous media. Scheidegger<sup>5</sup> in his excellent book criticises this equation very carefully, indeed. Unfortunately, I could get it only after my paper was finished.

<sup>5</sup> Scheidegger, A. E., *The Physics of Flow through Porous Media* (University of Toronto Press, 1960)