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FUNDAMENTALS OF BARRIER PROPERTIES

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Synopsis The fundamentals of barrier protection of both porous materials and of intact polymer films and coatings are outlined. The importance of the elimination of even small pinholes is demonstrated and comparisons made under various conditions of protection such as changes in humidity and the presence of vacuum or air at the low concentration side.

The types of paper, board or glassine substrates is discussed, together with their influence on the protective properties of the barrier. The design of the polymeric coating on its permeability properties when free from pinholes is discussed in detail and the molecular and other factors are related to the performance of the barrier. Crystallinity, the glass transition temperature, orientation and cross-linking and their effect on gas and vapour barrier properties are also reviewed. In addition, the possible differences between coatings deposited from latex, melt and solution are considered.

Finally, it is pointed out that the nature of the substance against which protection is needed is highly important and a polymer which is an excellent water vapour barrier might be a poor grease or organic vapour barrier and vice versa. Some newer developments in the barrier coating field are also presented.

Introduction

PAPER itself provides comparatively little barrier protection to the passage of gases, water vapour, oils, grease and other chemicals. Its use in packaging and other applications (when barrier properties are important) hinges therefore on the successful applications of coatings or resort to lamination with high barrier materials. Although metal foils in combination with a suitable adhesive can be and are used, most of the modern barrier materials are either waxes, wax-polymer combinations or (more usually) organic high polymers such as polythene. The discussion in this paper will deal mainly with these organic polymeric coating and laminating materials. In particular, the factors that affect the performance of these barrier materials, including the paper substrate itself, will be discussed in some detail. This may seem a disappointingly narrow approach to some, but it is the area in

Under the chairmanship of Prof. M. F. Judt which most fundamental work has taken place and most advances have been made.

The barrier properties are usually described in terms of a *permeability constant*, which in general is the proportionality constant between the flow of penetrant per unit area of barrier per unit time and the driving force per unit thickness. In most practical barrier problems concerned with gases and vapours, the pressure difference is the normal driving force considered, but the exact meaning and significance of the permeability constant depends on the mechanism of transport that is operating. These various mechanisms will be considered in the following section.

Mechanism of barrier protection

Two distinct mechanisms for permeation through coated papers are readily apparent. These are (*a*) flow through actual pores, capillaries, pinholes and other defects; (*b*) activated diffusion through intact polymer films. In principle, a combination of both mechanisms may be operative or one or the other may predominate according to the temperature and/or other conditions. These situations will be discussed further in subsequent sections. Each class of permeation will be discussed separately in this treatment.

Flow through pores

Many mechanisms of pore flow have been distinguished according to the pressure, pore diameter, barrier thickness, temperature and other parameters. These have been treated in great detail by Barrer(1) and by Carman.(2) In most practical barrier situations, the flow is normally of either the viscous, Poiseuille type or interdiffusion, when the pressure generally is similar on both sides of the barrier.

Viscous flow—The simplest of flow mechanisms is viscous flow, in which the volume of penetrant q passing through a capillary of radius r and length Δx in unit time is given by Poiseuille's equation (*1*)—

$$q = \pi r^4 \Delta p / 8 \eta \Delta x \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where η is the viscosity of the permeant and Δp is the pressure drop across the capillary. The permeant flow per unit area of capillary and per unit time is therefore given by—

$$q / \pi r^2 = \beta r^2 \Delta p / 8 \eta \Delta x \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where β is a tortuosity factor that increases the effective length from Δx to $\Delta x / \beta$. Hence, the membrane flux can be given as equation (*3*), where ϕ is the volume fraction of capillary in the membrane.

$$q = \frac{\varphi\beta r^2}{8\eta}\frac{\Delta p}{\Delta x} \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

Accordingly, the permeability coefficient P discussed previously corresponds to equation (*4*). For all penetrants that do not interact with the membrane, that is, for which—

$$P = \varphi\beta r^2/8\eta \qquad . \quad . \quad . \quad . \quad . \qquad (4)$$

ϕ and r are independent of the penetrant and the permeability coefficients are inversely proportional to the viscosities of the penetrant.

The viscosity of gases is directly proportional to temperature and, accordingly, permeability of gases through porous media such as glassine shows a small, but negative temperature dependence.

For liquid permeants, viscosity is generally inversely proportional to temperature and the temperature dependence is positive. In liquid permeation, the pore radius is often calculated by assuming that the flux goes only through the capillaries and the volume fraction of fluid in the entire membrane is the volume fraction of capillaries. The equivalent pore radius so obtained may. serve as a parameter for characterising membrane permeability. It should be borne in mind, however, that such numbers arise from a hypothetical model of membrane behaviour and may not correspond to physical reality.

When permeation occurs by a flow mechanism, the pressure drop across the membrane is the driving force regardless of the phase of the penetrant—that is, whether it is a gas or a liquid.

An idea of the flow that occurs by the Poiseuille mechanism can be gained by considering the case of a one atmosphere pressure difference of oxygen through a single one micron radius hole in a one mil film at 25° C. Here, equation (*1*) can be used in the simplest case and q becomes equal to $7{\cdot}2 \times 10^{-5}$ cm^3 per second.

A calculation of the Reynolds number shows it to be extremely small in this example and the equation used is therefore indeed reasonably correct.

Interdiffusional flow—In many practical barrier problems, there is no pressure difference, but only partial pressure differences. A good example would be a package such as a sugar envelope. Here, there is roughly one atmosphere total pressure on both sides of the barrier, but the water vapour pressure could be, say, 20 cm Hg on one side (about 80 per cent relative humidity at 25° C) and essentially zero on the other side.

Here, q = Area × Free diffusion constant × *relative pressure*/thickness

$$\text{that is, } q = \frac{A.\ D.\ p(\text{partial})}{\Delta x\ p(\text{mean})} \qquad . \quad . \quad . \quad . \quad . \qquad (5)$$

In the example used previously (a one micron radius hole in a one mil film), q becomes equal to $7 \cdot 6 \times 10^{-8}$ cm³ per second. It is interesting that calculations show the interdiffusion constant leads to about a sixfold reduction in the flow of water vapour compared with the corresponding vacuum situation.

Activated diffusion

The transmission of a gas or vapour through a polymer film in the absence of cracks or pinholes is of the activated diffusion type. That is to say, it is a process in which the gas or vapour dissolves in the film at one surface, diffuses through the film under a concentration gradient and evaporates from the other surface at the lower concentration. It can be seen, therefore, that the rate of transmission depends on the solubility of the gas in the film at a given pressure and on the diffusion constant of the dissolved gas in the polymer.

Under steady-state conditions, the rate of flow of the gas may be expressed by Fick's law—

$$q = -D(\partial c/\partial x) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where q is the amount of gas passing through a unit area of film in unit time, D is the diffusion constant and $\partial c/\partial x$ is the concentration gradient in the direction of flow. If D is independent of the concentration or position in the film, this expression may be integrated to—

$$q = D(C_1 - C_2)/l \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where C_1 and C_2 are the steady-state concentrations of gas in the inflow and outflow surfaces of the film and l is the film thickness.

The gas concentrations are usually expressed practically in terms of the pressures (p) of the gas above each surface and these quantities related by Henry's law—

$$c = S \cdot p \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where S is the solubility coefficient for the particular gas or vapour in the polymer in question.

Substitution in the first equation yields—

$$q = D \cdot S \frac{(p_1 - p_2)}{l} = P \frac{(p_1 - p_2)}{l} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where $P = D \cdot S$ is the permeability constant. This value is a constant at a given temperature when Henry's law is obeyed and the diffusion constant is independent of the gas concentration. This has been found to be true for the permanent gases and for carbon dioxide at all normal temperatures and pressures. Nearly all quoted gas transmission values are given in these terms for various units and values.

The normal units used for the permeability constants are cubic centimetres of gas at STP passing per second under a gradient of 1 cm Hg pressure per cm thickness and per square centimetre of area. Diffusion constants are in units of cm^2/s and the solubility coefficient in units of cubic centimetres gas at STP per cubic centimetre of polymer at 1 cm Hg pressure.

Since permeability constants in these units have values for most polymers in the range 10^{-7}–10^{-12}, many larger number units are used in practical application studies. The most common of these is in units of grams per square metre per 24 h under a given pressure or, in the case of water vapour, at a given relative humidity difference. The various units may readily be converted from one to another. Since permeability constants are often highly temperature-dependent, values are normally quoted at a given temperature. For organic vapours and often with water vapour, the permeability constants depend on the vapour pressures themselves and it is necessary to specify the exact conditions of measurement. This question will be discussed later in more detail.

Finally, let us calculate the resistance of an intact polythene film of one mil thickness with the two situations described above, but by the activated diffusion mechanism.

The permeability constant at 25° C for oxygen in low density (0·922) polythene is $5{\cdot}5 \times 10^{-10}$ and for water vapour is $9{\cdot}0 \times 10^{-9}$, both in units of cm^3 at STP per cm^2 per cm thickness per second under a pressure difference of 1 cm Hg.

For 1 cm^2 of film with one atmosphere of oxygen pressure difference, the rate of gas transmission $q = 1{\cdot}6 \times 10^{-5}$ cm^3 STP per second. With 2·0 cm Hg pressure difference of water vapour, the corresponding flux $q = 7{\cdot}2 \times 10^{-6}$ cm^3 STP per second. These results, compared with those calculated for a single one micron radius pinhole, give an idea of the relative importance of the pinholes. In the case of the oxygen transmission, the pinhole is the main source of flux, whereas for water vapour the film itself provides the main flux. It should be borne in mind, however, that the simple pinhole represents only about 3×10^{-8} per cent of the exposed area.

Effect of geometric and intensive variables

It is clear from the discussion of both the pore and the activated types of permeation that the permeabilities are, by definition, directly proportional to the area of the barrier and to the pressure difference and inversely proportional to the thickness. The pressure dependence of activated diffusive permeability can be very complex in the case of water vapour and organic vapours. The liquid values correspond with those for the saturated vapours.

This topic will be treated in more detail when water and organic vapours are discussed. The effect of temperature is also quite complicated. Often with pore flow, since the viscosity of a gas increases with increasing temperature, the permeability decreases. For activated diffusion, the temperature dependence of the permeability constant is represented by—

$$P = P_o \exp(-E_p/RT) \qquad . \quad . \quad . \quad . \quad (10)$$

where P_o is the pre-exponential factor, E_p is the total activation energy for permeation, R is the gas constant and T the absolute temperature.

$$P = D \cdot S \text{ (equation 8)}$$

$$D = D_o \exp(-Ed/RT) \text{ and } S = S_o \exp(-\Delta H_s/RT)$$

where Ed is the activation energy for diffusion and ΔH_s is the heat of solution. Consequently—

$$Ep = Ed + \Delta H_s \qquad . \quad . \quad . \quad . \quad . \quad (11)$$

Whereas the diffusion constants always increase with temperature, the permeabilities can, under certain conditions such as constant pressure, increase or decrease with increasing temperature.

Paper and bond as barrier substrates

PAPER and board when sized can provide a certain measure of resistance against aqueous solutions, but are not considered as barrier materials. They provide the structural protection and strength and the barrier coating itself provides the protection against gases, vapours, water, grease and other penetrants. Glassine, greaseproof papers and parchment are dense, smooth surfaced papers with only a small number of voids and pores. Being hydrophilic, they are resistant to capillary wicking and penetration by greases and oils. Their dense structure restricts the passage of gases and they are relatively good odour and aroma barriers. They are dense and lint-free and have comparative freedom from pinholes, which make them ideal substrates for coatings or laminations.

In the role of support material, the paper or board texture and density often determine the amount of coating required to achieve the intended result. For example, the coating should be applied to a smooth dense surface, as voids or pinholes in the coating will permit the passage of water, grease or the like as well as ruining the gas barrier performance. Likewise, any fibres protruding through the coating may serve as wicks permitting passage of the specific material through the coating. These comments are applicable equally to laminates, except that a greater amount of material is usually necessary to achieve the same barrier properties, owing to the double hazard of wicking, pinholes and so on.

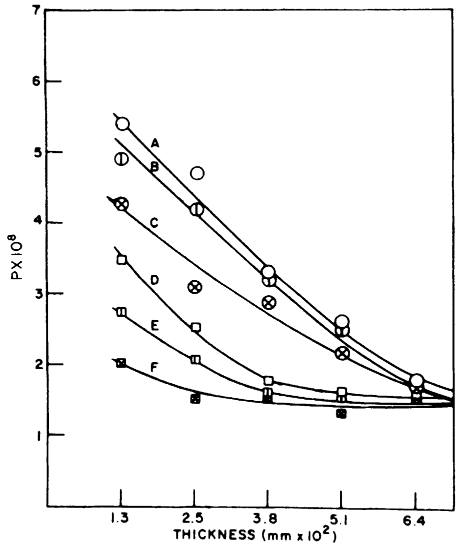

Fig. 1—Effect of coating thickness on water vapour permeability of polythene-coated kraft at 30° C (*P* calculated on polythene thickness only)

A Kraft exposed to humidity, 20 mm Hg vapour pressure
B Kraft exposed to humidity, 15 mm Hg vapour pressure
C Kraft exposed to humidity, 10 mm Hg vapour pressure
D Polythene coating exposed to humidity, 20 mm Hg vapour pressure
E Polythene coating exposed to humidity, 15 mm Hg vapour pressure
F Polythene coating exposed to humidity, 10 mm Hg vapour pressure

The effects of thickness is well illustrated in Fig. 1 for a carefully controlled series of polythene-coated kraft papers. It can be seen that, as the thickness of the coating increases, the water vapour permeability constant (normalised to 1 cm thickness) gradually decreases until it ceases to depend on the thickness and approaches that of the pure film. At the same time, the effect of wicking can be seen in that the water vapour permeability is greater when the paper side is exposed to the high humidity than when the polythene-coated side is exposed. In this case, the vapour pressure decreases before the wicks are reached and the wicks become less effective than when the paper is fully exposed to the humid atmosphere. Again, this effect disappears as the coatings become thicker and wicking becomes absent. The corresponding gas permeabilities did not show the two-sided effect, but did show greater permeabilities with the thinnest coated sample. This shows that pinholes as well as wicks are present in the very thin coatings. Similar thin coatings on glassine were found to be free from pinholes or, of course, wicking effects.

With production line coated papers, these effects are often masked by the changes in the polythene crystallinity and, consequently, the barrier properties with the change in the extrusion conditions. Thus, lightweight coatings tend to be more oriented and to crystallise more at the higher speeds used. Sometimes, if the coating is pressed deeply into the paper matrix, abnormally low gas permeabilities are found. The paper fibres themselves have negligibly low permeability and the coating, therefore, has effectively greater thickness when pressed into the paper.

Water vapour, on the other hand, can readily penetrate around the fibres and so water vapour permeability is normal for these coated papers.

Coated glassine

Glassine is, of itself, quite an effective gas barrier in the best sense because of the small number of pinholes present, though a good quality glassine would still, at room temperature, have only about one fifth the barrier resistance of polythene. Some typical values for glassine and polythene are presented in Table 1.

TABLE 1—COMPARISON OF PERMEATION BY CONVECTION AND ACTIVATED DIFFUSION

Gas	*Temperature, °C*	$P \times 10^{10}$	
		Glassine	*Polythene*
Nitrogen	0	11·2	0·25
	30	9·4	2·1
	50	9·3	7·4
	70	8·4	22·0
Oxygen	30	10·5	6·9
Carbon dioxide	30	9·7	28·1
Hydrogen sulphide	30	9·7	43·0

The table illustrates a number of important differences between flow through pinholes and activated diffusion through plastic films. In pinhole flow, the gases nitrogen, oxygen, carbon dioxide and hydrogen sulphide all have similar permeability constants, whereas the values vary greatly in activated diffusive flow. Hydrogen sulphide, for example, permeates twenty times faster than nitrogen does, mainly because of the greater solubility in the barrier of the more easily condensible gases such as carbon dioxide and hydrogen sulphide. This leads, in the case of the particular sample of glassine tested, to the glassine being a better barrier than an equal thickness of polythene for those two gases. The effect of temperature is also quite different for glassine and polythene. Increasing the temperature leads to a small decrease in the gas permeability of glassine, owing to the increasing viscosity of the gas; with activated diffusion, however, increasing temperature leads to greatly increased permeability and so the glassine becomes a more effective gas barrier than polythene at higher temperatures.

Factors affecting activated transport through polymeric barriers

General and gas permeation

THE rate of transport by activated diffusion through plastic films is governed by the permeability constant for the barrier material. It has been shown earlier (section on activated diffusion) that this is the product of the diffusion constant and the solubility coefficient. Any discussion of the permeabilities must concern itself, therefore, with both constants.

TABLE 2—THE PERMEABILITY OF VARIOUS POLYMERS TO OXYGEN, WATER AND CARBON DIOXIDE AT 30° C

Material	P_{O_2}	P_{CO_2}	*Ratio*	P_{H_2O}
Polyacrylonitrile	0·0002	0·0008	4·0	300
Polymethacrylonitrile	0·0012	0·0032	2·7	410
Lopac (Monsanto Co.)*	0·0035	0·0108	3·1	340
Polyvinylidene chloride	0·0053	0·029	5·5	1
Barex (Sohio Co.)*	0·0054	0·061	3·4	660
Polythene terephthalate	0·035	0·17	4·9	175
Nylon 6–6	0·038	0·16	3·6	275
Polyvinyl chloride (unplasticised)	0·045	0·16	3·6	275
Polyethylene (density 0·964)	0·40	1·80	4·5	12
Cellulose acetate (unplasticised)	0·80	2·40	3·0	6 800
Butyl rubber	1·30	5·18	4·0	120
Polycarbonate	1·40	8·0	5·7	1 400
Polypropylene (density 0·907)	2·20	9·2	4·2	65
Polystyrene	2·63	10·5	3·8	1 200
Polythene (density 0·922)	6·90	28·0	4·0	90
Neoprene	4·0	25·8	6·5	910
Teflon	4·9	12·7	2·6	—
Natural rubber	23·3	153·0	6·6	2 600
Poly-4, methyl-pentene-1	32·3	92·6	2·9	—
Poly-dimethyl-siloxane	605·0	3 204.0	5·3	40 000

* Nitrile copolymers

Units: cm^3 (STP)/cm^2/cm/s/cm Hg × 10^{10}

Both the diffusivities and the solubilities are affected by the nature of the penetrant and the nature of the polymeric material. In addition, any interaction between the penetrant and the polymer must be considered. If there are no interactions, the two penetrants would permeate through a polymer film in the same ratio, regardless of the nature of the polymer. In Table 2, the permeabilities of oxygen and carbon dioxide for a wide variety of barrier materials are listed, together with their ratios. It can be seen that the permeability constants vary across a three million fold range, whereas the ratios between those of oxygen and for carbon dioxide are all, essentially, within a factor of two of each other. This remarkable result shows the almost negligible degree of interaction between the barrier and gas molecules and enables one to predict one value if those of another gas are known. Water vapour and organic vapours, on the other hand, can interact strongly with the barrier material. This subject will be discussed later. Some of the factors that lead to the differences in permeability between different gases in the same polymer and the same gas in different polymers will now be considered.

Nature of the penetrant—The *solubility* of the penetrant will be greatly affected by its polarity or its cohesive-energy density and the similarity of these quantities with that of the polymer. This relationship may be regarded as a more quantitative expression of the well-known adage 'like dissolves like'. It is clear, for example, that a hydrocarbon such as n-hexane should have higher solubility in polythene than, for example, methyl bromide and this is indeed the case. It should be borne in mind that cohesive-energy densities are often similar for materials of quite different structure. Thus, chloroform, methyl ethyl ketone and styrene all have similar values for their cohesive-energy densities; the actual values should be consulted before conclusions are drawn about the possible solubility effects. Cohesive-energy densities are usually listed as their square roots—that is, as solubility parameters. For gases, solubility in polymers has been satisfactorily correlated with boiling points and critical temperatures and with Lennard-Jones force constants.(5) As would be expected, the more easily condensable gases are more soluble.

The *diffusivity* of a penetrant depends mainly on its size and shape and numerous attempts have been made to put this relationship on a more quantitative basis. The data for the simple gases shows a scattered relationship between the energy of activation for diffusion and the first and second power of the molecular diameter. For organic molecules, the shape factor becomes highly important—for example, a planar molecule such as benzene has a much higher diffusion constant than a spherical molecule of similar diameter such as carbon tetrachloride. Similarly, branched hydrocarbons diffuse more slowly than do their linear counterparts.

Nature of the polymer—The *solubility* of a penetrant in a polymer depends on the similarities in their cohesive-energy densities. The nature of the polymer structure (that is, its morphology) can also be important. With semi-crystalline polymers, solubility occurs only in the non-crystalline regions and the solubility is roughly proportional to the amorphous content. With highly drawn polymers, other factors are involved and the order of solubility of a series of solvents can sometimes be changed in that the size and shape of the penetrant may become the governing factor. Cross-linking, in general, tends to reduce solubility with the more highly swelling penetrants, but otherwise has little effect except at very high degrees of cross-linking.

The *diffusivity* of a penetrant in a polymer can best be interpreted in terms of the Eyring picture of viscosity or diffusion. The polymer can be visualised as a tangled mass of polymer chains with the holes between them. At normal temperatures, there is considerable segmental mobility and the holes are continually forming and disappearing as a result of thermal motion. Diffusion of a penetrant takes place by a succession of jumps from hole to hole under the influence of the gradient of concentration or, better, the chemical potential. The energy of activation for diffusion can then be related to the cohesive energy of the polymer—the energy associated with hole formation. The pre-exponential factor of the diffusion constant, on the other hand, can be associated to some extent with the number of holes or looseness of the polymer structure, the free volume.

The effect of crystallinity on the diffusivity is quite complex. In general, the crystalline regions interrupt the flow lines and lead to increased tortuosity of the diffusion path. In addition, the crystallites act as cross-links restraining the mobility of the chains. These two effects have been studied by Michaels and co-workers;(5–9) the former effect is by far the most important. The dependence of the diffusion constant on the amorphous content is complex. For some polymers such as poly(ethylene terephthalate), it is first-power dependence; for certain grades of polythene, it is almost second power. This, coupled with the linear dependence of the solubility on the amorphous content, leads to a general dependence of the permeability constant on the second to third power of the amorphous content. The amorphous content is roughly proportional to (1 − density) and Alter(10) has shown for a large number of polyethylenes of different densities that the permeabilities of gases vary with $(1-d)^{2\cdot 1-2\cdot 2}$. Very useful practical correlations are presented in this paper.

Cross-linking has a small effect on the diffusivity. For example, one cross-link per about thirty monomer units of polythene leads to a reduction of the diffusion constant by one half.(3)

It is difficult in comparing the relative permeabilities of a series of polymers to clarify the role of the various factors that contribute to the observed differences, but a consideration of the variables discussed briefly above can help in predicting the permeation properties of a polymer with fair accuracy.

Permeability to organic vapours

The permeation of organic vapours has already been discussed in some aspects. Unlike the permeability to gases, there is a pronounced interaction between the penetrant and the polymeric barrier. This is characterised by a definite increase in the rate of permeation with the vapour pressure, owing to the increased concentration of the penetrant in the film. This, in turn, leads to plasticisation of the film and a consequent increase in the diffusivity. In addition, the solubility of the penetrant increases with pressure in an approximately exponential compared with a linear (Henry's law) fashion. Consequently, the permeation increases sharply with vapour pressure.

The permeability of polymer films to organic vapours is obviously complex. It is also an important factor in many practical packaging and other applications. The actual rates of permeation depend, of course, on the particular organic material involved. A useful empirical relationship between the structure of the organic penetrant and the permeability has been developed by Salame(11) for the practical prediction of the permeability.

The equation developed is as follows—

$$\log P' = K - 0{\cdot}22\pi$$

where P' is the permeability factor in units of (g) (mil)/(24 h) (100 in^2), π is the permachor and K is a constant related to temperature T (in °K) as seen in the equation $K = 16{\cdot}55 - 3\,700/T$.

The permachor values for polythene are listed in Table 2 and are simply additive for calculating the permachor of a particular compound. The permeabilities of a large number of organic materials through polythene have been measured and compared with those calculated from the permachor values with reasonable agreement in most cases.(11)

Permeabilities to water vapour

The permeation of water vapour is extremely complex compared with the behaviour of gases.(12) From the strictly practical point of view, only two cases need be considered—(*1*) the permeability constants vary linearly with the water vapour pressure and (*2*) the permeabilities increase sharply with vapour pressure, owing to the plasticisation of the barrier film by the absorbed water. This latter situation is also manifested by an increase in gas permeability with increasing relative humidity. In fact, even the pressure independent permeability is highly complex in that the diffusion constant can actually decrease with concentration of water in the film due to 'clustering' of the water molecules in the polymer. This phenomenon will be discussed further in the subsequent section. In any event, the permeation of water vapour does not follow the simple relationship shown by the gases. This is illustrated by the data in Table 2, where the permeabilities of a number of barrier films to water vapour are included. It can be seen clearly that low gas permeability does not in any way imply low water vapour permeability. This is almost always because of the change in the solubility coefficient, which can be said in a sense to be due to the interaction between the penetrant (water in this case) and the polymeric barrier. Thus, in the case of a strictly hydrocarbon polymer like polythene, even the high density material has more than ten times the oxygen permeability of polythene terephthalate. The corresponding water vapour permeability is quite different, however, being about fifteen times greater in polythene terephthalate than in polythene. In fact, water vapour permeates thirty times faster than oxygen in polythene, but five thousand times faster in polythene terephthalate. Thus, the simple relationship found with gases (for example, 4·9 compared with 4·5 for carbon dioxide and oxygen for our two polymers) breaks down completely in the case of water vapour. On examining the components of the permeability constant, it is seen that the diffusivities for water vapour are quite similar in both polymers to those for oxygen. This is not unexpected, as the molecular diameters are not greatly different for these two penetrants. Thus, the differences in the barrier properties of these two films to water vapour are seen to be due overwhelmingly to the differences in solubility, which is due in turn to the degree of interaction of the penetrant and the polymer. In other words, the solubility coefficient of water in the comparatively polar polythene terephthalate is many orders of magnitude greater than that for polythene.

TABLE 3—SOME SELECTED PERMACHOR VALUES*

Atom or group	*Permachor value for atom or group*†			
	n = 1	*n = 3*	*n = 5*	*n = 7*
Carbon (—CH_2—)	1·0	1·0	1·0	1·0
Chlorine	1·2	1·2	1·2	1·2
Bromine	3·0	3·0	3·0	3·0
Sulphur	4·0	4·0	4·0	4·0
Nitrate	15·4	13·4	13·4	9·6
Ether		2·4	2·4	1·4
Ester		9·6	7·0	7·0
Ketone		10·8	8·5	8·5
Aldehyde	17·8	12·0	9·5	8·0
Anhydride		15·8	18·0	18·0
Amide	18·0	18·0	18·0	18·0
Amine—				
Aliphatic	6·0	6·0	6·0	6·0
Aromatic				11·0
Alcohol—				
Aliphatic	16·5	15·5	14·0	11·0
Aromatic				13·0
Acid—				
Aliphatic	18·0	13·5	11·0	11·0
Aromatic				14·0
Alicyclic	....add 1·0 below 80°, 2·0 above 80° F....			
Iso-substituted and side-branching	.... add 2·0			
Double bond between carbons	.... subtract 0·2			

* Additional values can be found in Salame.(11) These values are additive to calculate the permachor of a given compound

† *n* = number of carbon atoms in molecule

Recent advances in barrier technology

SINCE the publication of the TAPPI monograph(3) on permeability in 1962, a large number of papers have been published in the field. In general, however, the picture presented then differs little from what we know today. Most of the more recent theoretical developments have been concerned with anomolous diffusion of organic vapours through glassy polymers. Such transport is often accompanied by the formation of actual cracks in the polymer films, owing to the swelling forces created by the rapid sorption process. Progress in this field has recently been summarised by Hopfenberg & Stannett.(13) A number of ingenious methods have been developed for the determination of gas and vapour permeabilities. In particular, the use of thermal conductivity to measure permeabilities under isobaric conditions has been developed(14–15) and shows considerable promise. The permeability constants of a number of newer polymers have been measured in addition to studies of the effects of polymer morphology on gas and vapour transport. The work of Vieth *et al.*(16) with polypropylene is particularly useful and interesting in this field, as is the work on the effect of the deep drawing of polythene on vapour permeability by Peterlin *et al.*(17–19)

The particular complexity of water vapour has already been mentioned. Considerable new work has been reported and confirms the clustering hypothesis advanced many years ago by Rouse,(20) Zimm & Lundberg(21) and by Yasuda & Stannett.(20) An up-to-date summary of advances in the field of diffusion and permeation of gases and vapours in high polymers has recently been published(23) and an up-to-date tabulation of all known permeability constants has also been presented.(24)

In the field of new and tighter barrier materials, an outstanding development has been the use of acrylonitrile and methyacrylonitrile copolymers.(25, 26) These have extremely low gas permeabilities, although their water vapour permeabilities are too high for many applications. Developed originally to replace glass for beverage bottles, they are now being studied for film and coatings. Permeability values for a number of these new polymer systems are included in Table 2. Used alone or combined with other polymer films or grafted or deposited to and on other films and coatings by ultra-violet, plasma or other means,(28) excellent new barriers should be possible, using nitrile-containing monomers. Industrial developments in this area should be forthcoming within the next few years.

Finally, with the growing use of coating with polymers in latex form, work is needed to understand the difference between coatings deposited from latex compared with solvent, extrusion or hot melt coatings. An interesting paper by Vanderhoff, Bradford & Carrington has recently been presented.(29) It demonstrates clearly that there is a very slow coalescence of the polymer particles and that the water vapour permeabilities then approach the values of the pure polymer films. In some cases, many days' ageing are needed, however, for the complete water vapour barrier protection to develop.

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Transcription of Discussion

Discussion

Chairman The coating of paper is an ancient art—the Chinese did it 2 000 years ago (surface pigmenting their paper), also the Turks in the 15th and 16th centuries (treble treatment). Machine coating was introduced in this country for the first time in the sixties of last century. Now the surface treatment of paper and board is a growth industry, with web widths on or off the machine up to 10 m for printing papers on an airknife coater and speeds up to 1 000 m/min on a blade coater. What is our scientific understanding of these paper treatments after doing them for the last 2 000 years?

Prof. B. G. Rånby I have one comment about the possibilities of making paper less permeable. As pointed out by Prof. Stannett, the only reasonable way is to put a coating on as a continuous surface layer. Any attempt to disperse particles or latex in the fibre suspension or impregnate the paper to decrease permeability are much less effective.

There is one more point I wish to make related to the problem of having polymers other than those now commercially used to decrease the permeability by surface coating. The new polymers that have been brought on to the market recently—plastics like Barex and Lopac containing acrylonitrile—are very impermeable, they have a high mechanical modulus and they can also be used within a wide temperature range, which makes them favourable as packaging materials. It has also been stated that these new materials have advantages from an environmental point of view: we have to be careful there. PVC develops hydrogen chloride when burned, which is not really poisonous, although it is an acid. We must look also at the burning of the acrylonitrile polymers: at low temperature with insufficient oxygen, they give hydrogen cyanide, which *is* poisonous. If you burn at high temperatures with an excess of oxygen present, these plastics develop nitrous oxides, which are rather detrimental to the environment. The same is true for other polymers containing nitrogen—polyamides, polyurethanes and native products like leather and wool. We have to define the burning conditions carefully for temperature and oxygen flow to prevent formation of poisonous and otherwise undesirable gases.

Under the chairmanship of Prof. M. F. Judt

Mr J. R. Parker I would like first of all to thank Dr Youngs for so kindly talking to papermakers about this rather complicated subject. I think his approach is of great value and this will become more apparent in the further papers to be presented.

Here, we have in fact a macroscopic measure of the behaviour of fluids in unsaturated porous materials. This has great advantages over the approach for which a model is needed. This is not to say that models are not of great interest and importance, but here is a means of describing the movement of liquids without making any assumptions about the nature of the material.

Dr Youngs' approach also gives the answer to a question posed by Dr Tollenaar many years ago, 'How can we explain the distribution of oil up a strip of paper during a capillary rise experiment?' He had to do this in terms of a rather complicated model based on interconnected capillaries. This experimental result, as we see now, can be subjected to quite a different sort of treatment and useful information can be obtained for application to other problems. This approach is relevant to the setting of inks on printing papers.

May I say a word of appreciation about Dr Oliver's contribution. His work reveals phenomena that are of great importance in the printability field.

Dr J. D. Peel Mr Gate, referring to your graphs from the mercury porosimeter apparatus, did your analysis of the results take account of the effect of the pressure of the mercury on the pore size distribution in the clay? The pressures were fairly high and would probably alter the pore size distribution as the experiment progressed.

Mr L. F. Gate This is quite a valid point. My answer to it is that we only get to about 20·7 MPa (3 000 lbf/in^2), which may sound a lot, but the local distribution of pressure inside a coating will in fact be much less than that.

We have also looked at the forces necessary to disrupt a coating by using the Talystep. By increasing the loading on the stylus, a point is reached when you begin to disrupt the coating and a track is left behind as the stylus passes over it. From this, you can, from the loading on the stylus, the area of contact and the time of contact, get an estimate of the forces necessary to start disrupting the coating—and these in fact work out to be something of the order of 69 MPa (10 000 lbf/in^2). By the fact that you can get pool values that agree with other methods, using materials you might expect to be crushed, you could come to the conclusion that it is not particularly important, as the local variation pressures within the coating under the intrusion pressures are not great.

Discussion

Dr E. L. Back With respect to both papers by Dr Youngs and Mr Gate, it might be appropriate to say a few words about the directional anisotropy of pores in paper. It means comparing the porosity and flow restriction in the Z-direction with that in the sheet direction. One way to quantify this comparison is by the effective pore radius for capillary flow by the Lucas-Washburn equation in these two directions. Fig. J shows the ratios of these two effective pore radii, that in the Z-direction divided by that in the machine-direction, for boards over a range of densities. These are rather thick boards made on Fourdrinier machines and the layered structure of paper increases this anisotropy. The ratio for the papers we tested is in the range of 0·01–0·04.

In these measurements, the same liquid is used in both directions, so the wettability does not enter this ratio. We found this to be true when we compared oil and water, so long as the papers were unsized or free from inherent resin.

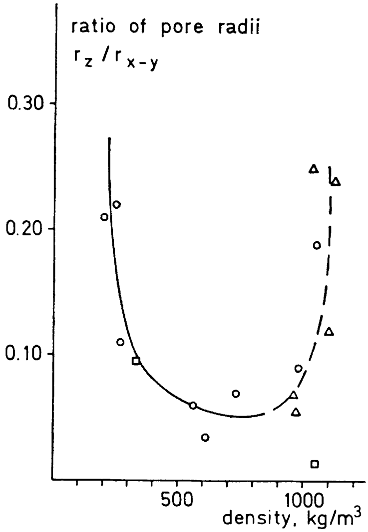

Fig. J

The ratios in this case were the same, within ± 10 per cent. For sized papers and papers with a large amount of mechanical pulp with inherent resin(such as newsprint), even if a surface agent was added, the ratios fell another one or two decades with water compared with oil. This might indicate that there is an additional anisotropy superimposed when resin or rosin is added to the paper. The distribution of this oleophobic compound will thus change the pore anisotropy.

Pore anistropy is important when evaluating the paper by impregnation, as well as for all printing.