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PERMEABILITY OF FLEXIBLE MATERIALS USED IN FUEL STORAGE TANKS: PART 1 - GENERAL REVIEW

B.C. Ennis

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A review of the transport of hydrocarbon fuels through composite elastomer-coated fabrics has been undertaken in order to identify critical factors that affect the design of the fabrics and the selection of materials. Specific areas of future interest are nominated.

Although the review was completed several years ago, the principles enunicated are still valid.

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ABSTRACT

A review of the transport of hydrocarbon fuels through composite elastomer-coated fabrics has been undertaken in order to identify critical factors that affect the design of the fabrics and the selection of materials. Specific areas of future interest are nominated.

Although the review was completed several years ago, the principles enunicated are still valid.

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(Continued)

PERMEABILITY OF FLEXIBLE MATERIALS USED IN FUEL STORAGE TANKS

1. INTRODUCTION

A suitable method for monitoring the permeability of POL* tank fabric to test fluids over a limited range of temperature and pressure was requested. A previous survey [1] was insufficiently detailed to define the physical requirements and restraints for such a method, or to indicate possible extensions beyond specification testing that might be required.

The permeation of these fabrics by liquids can be described as pervaporation:- the liquid dissolves at one side of the polymeric membrane, diffuses across it under the influence of the concentration gradient and evaporates from the other side. The process is complicated by the use of mixed liquids and the composite nature of the fabric, which comprises a load-bearing synthetic fibre cloth coated on either side with elastomeric layers. Some fabrics use an additional impermeable plastic film, while others rely on the elastomers alone to afford sufficient resistance to diffusion of the contents. There are manufacturing advantages for the latter, but it is more difficult to achieve the desired impermeability [1] and consequently a clearer understanding of the factors affecting permeability of these fabrics would be useful.

Pervaporation is but one aspect of transport through (polymer) membranes; others which have received increasing attention over recent years include reverse osmosis (particularly for desalination), electrodialysis, haemodialysis, the possibility of separation of organic liquids by polymeric films, dyeing, and ion exchange chromatography. These are non-mediated processes, and should be distinguished from mediated molecular transport processes which commonly occur in biological situations and require a third substance (the carrier) to interact with the substrate and transport it

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* Petroleum, oil and lubricants.

through the membrane. Non-mediated transport results from the existence of a chemical potential gradient across the membrane. The gradient arises from concentration, pressure or activity differences, and attempts have been made to present a unified theory of non-mediated liquid processes [2] using the solution-diffusion concept which underlies most of the theories.

Because of the breadth of application and the varied technological approaches to liquid permeation through polymer membranes, complete coverage is unlikely to have been achieved in this review. The permeability of membranes to gases is simpler and better understood, and also perhaps has had more immediate relevance to such problems as those associated with (food) packaging and inner tubes for pneumatic tyres.

If a new method is developed and adopted for specification testing of the permeability of POL tank fabrics, it should offer clear advantages in terms of either procedural convenience, or amount and type of information obtained. In the latter case a definite application for either predictive or developmental purposes would be needed to justify developing a new technique.

The following is offered as a basis for discussion of the status of liquid permeation through composite membranes, and for definition of the requirements for an instrumental method. The discussion is maintained at a simple conceptual level and the detailed mathematical treatment should be obtained from the source material. Diffusional transport is assumed, and no consideration is given to percolation, i.e. flow through a porous medium.

2. DIFFUSION AND PERMEATION

Diffusion and permeation of polymers have been reviewed in detail in a recent monograph [3], and more specific aspects of permeation [4] have also been considered briefly. The major review of the subject relating to elastomers is more dated [5]. The theoretical treatment of diffusion is basically mathematical and should be approached from these sources (particularly [3] and [6]). The following treatment is not rigorous.

At a point in a homogeneous polymeric solid where there is a local concentration of a diffusing molecule, it can be shown that -

$$q = -D \frac{dc}{dx} \qquad (1)$$

where q is the transfer flux of the diffusant (per unit area),

$\frac{dc}{dx}$ is the lineal concentration gradient of the diffusant,

and D is the diffusion coefficient, or diffusivity of the polymer diffusant pair. Provided that flux and concentration are measured in the same (volumetric) units then D has the dimensions, length^{2}time^{-1}.

This is a simplistic expression of Fick's first law which is basic to diffusive flow through polymers.

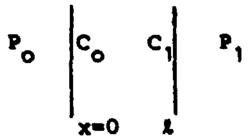
Fick's second law extends this consideration to the variation of concentration at a point with respect to time, and it can be shown that. for constant D, from consideration of mass balance:-

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} \qquad (2)$$

2.1 *Gas Diffusion*

The diffusivity of a permanent gas is independent of its (low) concentration in the polymer at any constant temperature. Once steady state permeation has been established for a membrane with the conditions shown,

$$\frac{dc}{dt} = o = D\frac{d^2c}{dx^2}$$



Thus the concentration gradient must be linear and

$$q = D(c_o - c_1)/l$$

It is assumed that the outer surfaces of the membrane are in instantaneous equilibrium with their environs - this is a critical assumption in all diffusion considerations - and since for a permanent gas with ideal behaviour, Henry's Law applies:-

$$c = Sp$$

where S is the solubility coefficient and
p is the partial pressure of the gas

and $$q = DS\ (p_o - p_1)/l$$

or $$Q = DS\ At\ \Delta p/l = P\ At\ \Delta p/l$$

where Q is total flow through membrane of area A in time t, and P, the permeability or permeability coefficiant, is defined by the product DS.

It is important to realise that P is not the "permeability" which is measured when testing POL fabrics to specification. In the latter measurement the thickness of the fabric is not considered and that property is therefore not intrinsic to the material but applies only the particular specimen.

When a permeant is introduced to one side of a membrane, then the rate of diffusing to the other side increases until the steady state is attained. Equation 2 can be developed to show that the time lag (θ), which is the extrapolated onset of steady flow, can be used to obtain D.

$$D = l^2/6\theta$$

The time lag experiment is popular because it gives both D and P (and hence S) in the one experiment. The major disadvantage lies in the difficulty in defining θ, particularly for thick specimens, and the need to allow adequate time (4θ) for equilibration has been stressed [7]. An alternative treatment using instantaneous diffusion rates rather than integrated flow appears to offer some advantage in the conduct of the time lag experiment [8].

The diffusivity can be determined separately by study of sorption kinetics as the diffusant is absorbed by, or desorbed from the polymer following a change of external concentration. Typically either the initial or final concentration of the sorbate is zero.

Thus provided that absorption and desorption at the surfaces is rapid compared to diffusive processes, and that Henry's Law is valid, permeation and diffusion are amenable to both theoretical and practical investigation. This is generally true for polymers (including elastomers) and permanent gases. The gases do not interact with each other, or the matrix, and mixtures of gases can be regarded as additive.

Difficulties can be encountered if the membrane material is not homogeneous, and for this reason permeability P should not be regarded as an intrinsic property [9] and D and S should also be determined. However the results of inhomogeneity can be calculated without difficulty and turned to advantage. The differences between the permeability of amorphous and crystalline regions in semicrystalline polyethylene have been utilised in the study of the morphology of deformed polyethylene films [10]. In a different context a model which allows for "trapping" of diffusing gas in microvoids has been used in analysis of the pressure drop in a pressurised plastic container [11].

2.2 *Condensable Vapours*

For condensable vapours the ideality of simple gases no longer applies, and it is probable that both the diffusion coefficient will be concentration dependent, and the vapour solubility in the polymer will be non-linear with respect to pressure.

If the diffusivity is solely determined by concentration then permeation is still amenable to analytical treatment; however if the diffusivity at a particular concentration is time dependent, then the behaviour is said to be "non-Fickian" and no analytical solution is possible.

Since D is determined by the local concentration, the value determined by any experimental method is the integral diffusion coefficient $\bar{D}$ for that concentration range and that experiment. It has been shown that

$\bar{D}$ (absorption) is generally greater than $\bar{D}$ (desorption), and that when the concentration dependence is not too great

$$\bar{D}_A = \tfrac{1}{2}(\bar{D}_{abs} + \bar{D}_{des}) \approx \bar{D}$$

It is postulated that the concentration dependence of D is such that

$$D = D_o\, f(c)$$

where D_o is the limiting diffusivity at zero concentration and f(c) is a function of c (f(c) = 1 when c = 0).

Then, for permeation between concentration c_o and c_1,

$$\bar{D} = \int_{c_o}^{c_1} D\, dc \,/\, (c_o - c_1)$$

$$= D_o \int_{c_o}^{c_1} f(c) dc/(c_o - c_1)$$

Thus by determining the integral diffusion coefficient $\bar{D}$ at various concentrations, it is possible to determine graphically both D_o and f(c). Simple empirical relations have been established, eg f(c) = (1 + αc) and $f(c) = e^{\alpha c}$.

In steady state permeation

$$q = -D \frac{dc}{dx}$$

$$\text{ie} \int_0^l q\, dx = -\int_{c_o}^{c_1} D\, dc = -D_o \int_{c_o}^{c_1} f(c)\, dc.$$

and the calculated $\bar{D}$ should be independent of specimen thickness. Similar considerations applied to sorption experiments indicate an independence of $\bar{D}$ from the film thickness [3c], and this is one of the tests for Fickian behaviour. Thus provided that the conditions are specified, values of $\bar{D}$, $\bar{P}$ and S_c can be defined such that

$$\bar{P} = \bar{D} \times S_c$$

$$\text{and } Q = \bar{P}\ tA\, \Delta p/l$$

but the relation is of limited use since the significant descriptive quantities are $\bar{D}$ (or more particularly D_o) and S_c, rather than their product.

The actual diffusion coefficients used are important, since absorption of the diffusant causes swelling of the polymeric network. The mutual diffusion coefficients used here calculate the concentration in terms of dry weight of the polymer, however it should be remembered that other diffusion coefficients can be used [3 a,c].

Permeation and diffusion of vapours in polymer membranes have not been treated in the same detail as those of simple gases. For quantitative (empirical) studies the diffusion coefficient must depend on concentration alone, and this is generally satisfied by elastomers above the glass transition temperature Tg [3c]. Below Tg, the polymer relaxation time scale can be commensurate with that of diffusion, and instantaneous equilibration to changed permeant concentration may not be achieved. The possibility also exists that in a cross-linked system swelling sufficient to cause bond rupture could cause time dependent behaviour.

The possibility of "clustering" should also be considered. It has been shown [3c], that association of diffusant molecules, particularly water, can occur and that the aggregate so formed can have different diffusive properties to the unassociated molecules. Although this is less likely for non-polar diffusants, it has been shown that there is a degree of clustering of xylene in polyethylene - presumably because the first molecule in the polymer network facilitates the entry of subsequent diffusant molecules near it [12a]. In this latter case the effect on diffusion is considered to lie in concentration anomalies rather than molecular aggregates.

2.3 Liquid Diffusion

The diffusion of liquids through polymer membranes is, in principle, no different from that of condensable vapors. The practical distinction lies in the fact that the permeant concentration at the upstream (ingoing) face is constant and equal to the equilibrium concentration or solubility (S_e) of the liquid in the membrane.

Thus for pervaporation, in the steady state, it can be written

$$Q = \bar{D}_e \, S_e \, At/l$$

$$= \bar{P}_e \, At/l$$

$$\text{i.e.} \quad \bar{P}_e = \bar{D}_e \, S_e$$

The formal similarity of this expression to that derived for simple gases is deceptive since S_e represents an actual concentration, not a solubility coefficient, because the pressure term is absent.

Provided that there is no time dependance, the integral diffusion coefficient $\bar{D}_e$, for the concentration range S_e to 0, can be empirically related to D_0 by vapor phase experiments, or by using partition of the permeant between the membrane and an inert (insoluble, non-diffusing) liquid. When there is time dependent behaviour, than although the same formal equations can be written, they would have even less significance, since "$\bar{D}_e$" is no longer independent of the specimen thickness, l.

2.4 *Membrane Types*

The state of material is important in this molecular transport.

(a) Glassy amorphous polymers. At temperatures below Tg, relaxation of the polymer molecule may be rate-controlling in the initial stages and considerable stresses can be induced between the swollen and unswollen parts of the membrane which lead to stress cracking (see, for example, [13]).

(b) Semicrystalline polymers. Transport generally takes place in the amorphous regions rather than the crystalline region. The permeability can be used to investigate morphology [10], however it has been suggested [12a] that time-dependent behaviour can be attributed to pulling out of edge molecules of crystallites during swelling. The analogy has been drawn between cross-linking in elastomers and the existence of crystallites in semi-crystalline polymers [12c], particularly in relation to stress relaxation effects.

(c) Elastomeric systems above Tg. These are generally thought to conform to Fickian diffusion. However, bond rupture on high swelling can induce a time dependence.

(d) Filled systems: there has been little published on these.

2.5 *Pressure and Liquid Permeation*

The previous theory indicates that, provided the equilibrium solubility of the permeant is unaffected by hydrostatic pressure, and if only diffusive processes occur, then the permeability should be independent of pressure. In highly swollen membranes, under the conditions of "hydraulic" permeation (reverse osmosis), the solvent flow is much greater than that predicted on conventional considerations for a diffusive mechanism alone, and an additional mechanism, viscous flow, is invoked [14b].

$$\text{i.e.}\quad Q = Q_{DIFF} + Q_{VISC}$$

Paul and Ebra-Lima [15] contend that for highly swollen homogeneous membranes this discrimination is unnecessary, and that the entire process may be attributed to Fickian diffusion.

The equilibrium concentration of solvent in a polymer is independent of applied hydrostatic pressure, and consequently so is the concentration at the upstream face of the membrane. Since the pressure is constant within the membrane [15a] flow must occur as a result of concentration changes: it is shown that as a result of the pressure differential compaction occurs at the downstream face. This concentration change at the downstream face is deduced from irreversible thermodynamics, rubber network theory and polymer solvent interactions. The range of concentration is not great and hence D is effectively constant. Paul introduces a "correction" to allow for the "frame of reference" appropriate to a swollen immovable membrane. Peterlin [14a] vigorously disputes the proprietry of the approach, but admits that apparently good correlations are obtained.

One consequence of this theory is that the pervaporative flux should be the limiting hydraulic flux at an infinite pressure difference [15 a,b], and fair agreement is obtained. In the examples given the total flow at 5 psi appeared to be about 2% of the pervaporatove flux for toluene/natural rubber. It would appear therefore that mass (or viscous) flow through POL tank fabrics should be insignificant compared to pervaporative flow.

The approach is valid only for homogeneous systems (i.e. those in which the polymer would dissolve in the permeant were it not for the crosslinks), and for constant D [15c]. [It is however important to distinguish between mutual diffusion, self diffusion and tracer diffusion coefficient [15 d,c,f] and to ensure that the appropriate frame of reference term is used). It is suggested [15f] that for swollen polymers D (mutual diffusion) is essentially constant over quite a wide range of concentration (polymer fraction volume 0.15 - 0.4 for natural rubber/toluene).

Since the inner lining for POL tank fabric is expected to meet a volume swell requirement of less than 50%, the compounds employed in it are by the above definition probably highly swollen.

Diffusion in a given membrane is considered to be hydrodynamic [15d] for volume fractions of rubber less than say 80%, i.e. it is considered that the diffusion characteristics in the rubber are determined by the viscosity of the liquid rather than of the rubber. This is in contrast to the more usual interpretation that at lower swelling the permeant dimensions and the polymer 'chain' mobility are controlling.

In summary, provided that the POL tank fabrics are non-porous there is no reason to suspect that small pressure differences will affect permeation rates within the accuracy expected, however theories deduced from hydraulic permeation are likely to be highly pertinent to understanding diffusive transport.

2.6 *Stress*

It has been shown for both semicrystalline [12 b,c] and elastomeric membranes [16] that the experimental procedure may set up restraints on the swelling of the sample at the upstream face (because of differential expansion) so that the unrestrained equilibrium swelling is not attained instantaneously. This time dependence of the upstream concentration would contravene Fickian diffusion, and would be particularly important in time-lag or sorption experiments. However if the induced stresses do not allow the normal equilibrium concentration to be obtained even steady state permeation will lead to erroneous results [12 b,c].

While this is essentially a practical point, it should be established whether or not the construction of the POL tank fabrics can modify the swelling of the coatings, and whether hoop or other stresses in the fabric may have more effect than simple hydrostatic pressure on permeation rates.

2.7 Rubber Formulation

There appears to have been very little reported on the effect of formulation on the diffusivity and permeability of elastomers, particularly to organic liquids. The diffusion studies have been mainly of gases [3d].

Petersen [17] studied oxygen diffusion in heterogeneous films comprising hard spherical polymer particles in a soft polymer matrix, and had some success using the Higuchi approach to diffusion in heterogeneous media

$$P_m = \frac{3 P_e P_i V_i + 2 P_e^2 V_e + P_i P_e V_a}{3 P_e + V_e (P_i - P_e)}$$

where P is the permeability and V the volume fraction, the subscripts m, i, and e refer to the mixture, the internal, and the external phases.

For an impermeable filler the equation reduces to

$$P_m = \frac{2V_e}{3-V_e} P_e$$

Chui [20] used this approach to study the diffusion of water in filled epoxy systems and concluded that there was an "immobilised" region of epoxy around the filler particles which effectively increased the volume fraction of filler (or tortuosity). This implied a decrease in solubility or permeability near the filler particles; the composite showed decreased permeability, and the analogy to "bound rubber" was advanced.

On the other hand Southern and Thomas [16] found that $\bar{D}$ was essentially insensitive to the level of HAF carbon black whereas the equilibrium sorption (S_e) was lowered by the presence of higher black loadings. The permeability (= $D \times S_e$) appears to decrease more rapidly than predicted by the above equation, however it was not determined directly by permeation.

The effect of plasticizers has not been studied except for gas diffusion [3b], and the effect of crosslinking is not clear. Much of the evidence suggests that D is decreased by increasing the level of crosslinking, particularly for gas diffusion. In relation to organic vapors there is evidence that the relation is not monotonic [3 c,d]. The diffusion coefficient of n-decane in natural rubber was not sensitive to a twelvefold change of crosslinking level while S_e changed twofold [16].

A study of the effect of filler loading and type (reinforcing and non-reinforcing, carbon and silica) on permeability, diffusivity, and solubility, and correlation with expansion coefficients, thermal conductivity, and 'bound rubber' for a representative rubber could offer interesting possibilities.

2.8 Laminated Construction

It can be shown that for ideal behaviour, the permeability of a laminated structure is defined by

$$\frac{1}{P} = \frac{1}{l} \Sigma \, \ell_{i}/P_{i}$$

where ℓ_i and P_i are the thickness and permeability of the i^{th} layer and l is the total thickness.

Barrie et al [19] have analysed the transient behaviour of 2 and 3 layer membranes with respect to the time lag experiment and the results were used to determine the structure of an oxidised rubber sheet. More recently Barrer [6] has considered some of the implications of laminated structures, and in a simplified form they have been used to determine boundary resistance and surface morphology [9].

However when non-ideal situations are considered the treatment is complex. Stannett [20] was able to show that for a nylon - ethyl cellulose laminate the permeability was determined by the direction of flow. He determined the flux for each layer of the laminate as a function of the partial pressure of the permeant (water vapor) and so was able to graphically determine the equilibrium flow.

Any prediction of flux through a laminate would therefore require a knowledge of the flux versus partial pressure of permeant (a more useful expression of concentration) for each layer. (The equivalent partial pressure is continuous at the interface whereas concentration is not).

If the permeability of the two layers is substantially different it is conceivable that $\bar{D}$ may be essentially constant in each layer, allowing useful approximations. Since Paul considered $\bar{D}$ to be relatively constant over a range of concentration for swollen rubber, a controlling resistant inner layer might be simply described. Numbers are necessary here.

A further problem with POL tank fabric resides in the fabric layer and its effect on permeation. If regarded as an air gap it would probably have little effect (D_{air} is large) [19] but this is most uncertain. Restriction of swelling of components may be more important.

There appears to be little if any published work on permeation of rubber/fabric composites. That reviewed [5] comprised contradictory references to balloon fabrics and dates from the zenith of that technology.

2.9 *Mixed Permeants*

The interaction of mixed liquid permeants in polymer membranes has received little attention. For simple gases with low solubility in the membranes there is nearly ideal behaviour, there is no interaction and each component permeates independently. The main emphasis has been on gas flow through (packaging) films under humid conditions; these are studies of effective plasticization, and increased permeability results from loosening of the polymer structure increasing D.

For a mixture of liquids (or vapours), if one component has negligible solubility and diffusivity in the membrane then it will merely influence the partition of the other at the ingoing interface, i.e. the concentration of the permeating one at the upstream face. This is also effectively true if there are major differences between the two permeants. Smith and Robeson [21] found that the more strongly absorbed butane controlled the permeability of polyethylene films to both components of an ethane-butane mix in the pressure/concentration range they studied.

Huang and Lin [22] found that the permeation of polyethylene by hydrocarbons could be described by

$$q = D_o (e^{\gamma c_s} - 1)/\gamma l$$

where γ is a "plasticization factor" and c_s is the solubility of the liquid in the polymer.

They compared the flux computed on this basis (having measured c_s) to the experimental flux of each component in a binary mixture. Augmented and diminished flow rates were found. This approach was extended to permeation of polar films by water and alcohols [23].

In liquid/liquid dialysis experiments [24] it has been pointed out that "time lag" measurements may reflect response to the dialysis solvent rather than the liquid "permeant", and that diffusional properties determined in this way may be very different from those determined by pervaporation. This is really an expression of the differing time to achieve steady state for fast and slow permeating components. There is also the possibility of either increasing or decreasing the steady state flow of the permeant in dialysis as compared to pervaporation as a result of plasticization or antiplasticization by the dialysis solvent.

Little has been reported on mixed permeants and elastomers, and (apparently) nothing on composite systems.

2.10 Temperature

Where there are no phase changes in the membrane and over a relatively restricted temperature range, it is generally found that S, P and D all follow Arrhenius temperature relations [3,4,5]. The significance of this has frequently been commented on and is important to the interpretation of diffusional mechanisms.

The Arrhenius relation has been found to hold for organic vapours [21], for solvent mixtures and components [22] and for (air) flow through composite membranes [19].

Paul [15a] has commented on the correlation of D and solvent viscosity, also noted by Southern and Thomas [16], and extended this to temperature dependence of both. He uses this to suggest that in swollen membranes the diffusion is "hydrodynamic" - i.e. controlled by liquid properties, rather than rubber properties [15d].

There are significant changes in diffusional properties at Tg (of the membrane) [3,5] but these are to be expected. More interesting is the report that they may not be monotonic with temperature in the region of the permeant boiling point [25], although this is not likely to be an important consideration for the POL tank fabrics.

It can be speculated that if the internal elastomer is (a) controlling the permeability of the POL tank fabric, and (b) swollen and in the hydrodynamic region, then useful empirical correlations may be possible.

3. MEASUREMENT OF PERMEABILITY

3.1 Methods

There are many methods for measuring permeability. Some of these have limited applicability, but in context a certain elegance. For example in studies of metallic sodium conductors the water permeability of the polythene insulation was evaluated from the change of resistivity of sodium filled tubes [28], a method unlikely to be widely adopted.

It has been shown that permeability is not an intrinsic property of materials, and is more properly considered in terms of diffusivity and solubility, particularly for heterogeneous materials. The sophistication of approach will thus dictate the general choice of method between the simplest steady state permeation experiment and the more informative kinetic approaches, either time-lag, permeation, or sorption and solubility experiments.

3.1.1 Permeation Methods

Change of weight is the most common method for measuring permeation of condensable vapours. The determination may be of the loss of permeant (as in POL tank fabric testing) or gain of permeant (water vapour transmission to dessicant) by a container sealed by the membrane of interest. Alternatively the permeant may be separately trapped in a suitable receiver downstream from the membrane. The advantage of the latter approach is that the composition can be subsequently determined by suitable means - GLC [22], refractive index [22], etc.

Volumetric measurement is possible if the permeation rate is sufficiently high and Paul [15] used precision tubing to measure flow through swollen membranes. The flux was high in this "hydraulic" permeation.

Pressure change is widely used for simple gas permeation, can be used for volatile liquids, and is usually used with a (near) vacuum on the down-stream side of the membrane. Thermal conductivity detectors, and titrimetric techniques, as well as the host of other chemical instrumental analyses can, and have, been used as appropriate.

Finally it should be noted that radio-tracer techniques have been used, these are most commonly used in time lag permeation and frequently in the absence of a concentration gradient of the unlabelled species. This tracer diffusion coefficient (and/or permeability) must be distinguished from the mutual diffusion coefficient more generally used.

These methods are suitable for both steady state and dynamic permeation experiments, although in the latter case it is possible to determine D from a plot of the instantaneous relative flux (without knowledge of the absolute rate) [27] and this may afford greater flexibility in choice of analytical method.

3.1.2 Sorption Methods

The kinetics of absorption (or desorption) are followed either by weight changes e.g. [16] or by dimension changes (swelling). The use of computer has allowed the use of more complicated evaluation of the kinetics of swelling [28] and the time dependence of D can be assessed. Sorption methods are not suitable for directional (vectored) materials like POL tank fabrics.

3.2 Experimental Design Considerations

3.2.1 Sensitivity

Present specifications require a maximum flux of 8 ml/m^2 day for POL tank fabric [1]. The flow through a circular sample of 5 cm diameter is thus 1.2×10^{-2} mg/min. For mixed solvents with minor components at the level of 5% the flux of an individual component may be of the order of

5×10^{-4} mg/min; 10% accuracy of measurement would require measurement of 50 ng/min.

It seems probable that this should be minimum flux to be measured, although thicker samples would restrict it further. While these flow rates could be detected by gas chromatography, they are near the limits of the technique - a typical GLC injection is about 0.5 µl, i.e. the total flow through the membrane for 1 h - and calibration would present difficulties at this level.

In-line analysis of the permeate appears to be impractical, and an integral method should be anticipated, in which the permeant is collected and subsequently analysed.

3.2.2 Membrane Support

For permeation of thin films some support of the membrane is necessary. It has been shown [12b] that the supporting element can have a significant effect on the measured flux, and the use of filter paper over a porous metal plate has been recommended. In the case of POL tank materials the fabrics are self-supporting, however it may be desirable to provide for later incorporation of this feature should the components be studied in isolation.

3.2.3 Pressure Differential

Because of the requirement that the permeant concentration at the dowstream face of the membrane should be effectively zero, it has been customary to construct liquid permeation cells with a vacuum at the downstream side. It has been shown that any restriction or restraint on the (swelling of the) membrane resulted in diminished permeability [12b] and consequently, although hydrostatic pressure is without effect on the theoretical permeability coefficient, more reliable and reproducable results were obtained when the non-permeant pressure differential was zero. The recommended apparatus used a vacuum on the downstream side, and liquid under its own vapour pressure only on the upstream side.

3.2.4 Pre-swelling

The effect of a positive pressure across the membrane was to hold it to the supporting plate and thus prevent full swelling. In the same way it was shown [12c] that the clamping of the membrane in the cell could delay and restrict swelling, and it was suggested that pre-swelling was desirable.

3.2.5 Soluble Material

The extraction and passage of material at the downstream side of the membrane will obviously lead to erroneous permeability. It should also be realised that extraction at the upstream side (particularly of low molecular weight polymer) can lead to increased solubilities of permeant in the membrane, and hence greater permeability [12c]. This can lead to a lack of correlation between vapour and liquid permeation experiments (because the vapour cannot extract). Pre-extraction of membranes is sometimes required.

In summary these practical considerations can be considered in terms of internal stress of the membrane. Similar effects can occur in sorption studies of semi crystalline polymers [12 a,d], and have been reported for rubber [16]. Additional effects can result from irreversible material changes - for example the pull-out and breaking of short or weak polymer chains between crystalline and amorphous regions of polyethylene, [12 a,d] and, by inference, crosslinks in elastomers. These effects should be distinguished from method based irreversibility.

Care should be taken to minimise these experimental stresses, particularly in the components, although it is recognised that they will be unavoidable in the fabric.

3.3 Suggested Principles of Apparatus

Experience with PCL tank fabrics has shown three practical difficulties which should be taken into account:-

- The specification requires an eight day test, and there is some doubt that the permeability is steady at this time.
- Distortion of the test disc occurs as a result of swelling.
- Difficulty has frequently been experienced in obtaining adequate sealing in the existing gravimetric method.

For these reasons a vacuum system, particularly at the upstream side, is likely to present difficulties and to obtain a zero pressure differential it is suggested that a two part cell should be used. The upstream side should be of similar dimensions to the current sealed cup, but provision could be made for circulation (and external heating) of the permeant. The lower section should provide for an air stream to sweep the face of the fabric to ensure rapid removal of the pervaporated permeant to the trapping/analysis system.

This approach has the following advantages:-

- The area can be well defined.
- Leakage from the upstream side should be no problem with light clamping forces, and would be irrelevant to measurements.
- Pressure on the upstream side can be minimised.
- The solvent can be flushed through without disturbance, thus ensuring constant composition and minimising stagnation. (a stirrer could be installed in the upper half of the cell).
- There should be constant air circulation at the downstream side.
- The fabric could be stressed in a suitable jig.
- Unattended operation would present no problem.

- The downstream section of the cell can be readily adapted (possibly with a soft o-ring) to collect permeate from the surface of an in-service POL tank - in this way a correlation between laboratory tests and tank performance could be made.

The major disadvantages foreseen are:-

- The membrane cannot be supported.
- Hydrostatic pressure may not be easy to maintain without leakage or membrane distortion.
- It seems doubtful that a suitable constant upstream vapour pressure can be maintained at atmospheric pressure for D_0 determinations.

The practical details of a suitable system have been considered in detail in Part II [39].

4. CONCLUSIONS AND RECOMMENDATIONS

Although there is an extensive literature on the diffusion and permeation of simple gases in polymers and elastomers, the emphasis in liquid diffusion has been on the specific areas such as dyeing, ion exchange polymers, or water vapor permeability. The more general considerations of liquid transport in elastomers, and particularly in heterogeneous system, has scarcely been touched.

It would be, I believe, inappropriate to embark on a programme of basic research into liquid diffusion in elastomers, however an empirical study of some aspects of composite fabrics and materials may be justified. Skeletal programmes are outlined below.

In particular, it is suggested that the state of knowledge of these materials is such that the value of a more sophisticated measurement (than the current gravimetric one) of permeability of existing fabrics is questionable, in the absence of concurrent investigational studies. The correlation of field and laboratory tests may go far to provide this justification, but it seems to me that some predictive ability for composite performance should be aimed for.

4.1 Development of Test Method

Aim: To develop a method for determining the permeability of POL tank fabrics and components. The method should operate with zero non-permeant pressure differential, allow analysis of permeate, and be applicable to both laboratory and field situations.

Material requirements: POL tank fabric, representative elastomer(s).

Significant variables: Temperature, fabric stress, possibly pressure.

4.2 *Permeability of POL Tank Fabric*

Aim: Empirical prediction of POL tank fabric performance from component properties and application data.

Material requirements: POL tank fabric and its separate components (elastomers, fabric, adhesives).

Significant variables: Elastomer thickness, laminate construction and symmetry, liquid composition, temperature, stress (hoop, hydrostatic).

Method: Mainly P, some D & S.

4.3 *Formulation of Elastomers: Effect on Fuel Permeability*

Aim: Correlation of permeability of elastomers with formulation variables and other physical properties.

Material Requirements: Polar and non-polar rubbers (e.g. natural, nitrile), fillers (carbon black, silica, reinforcing, non-reinforcing).

Significant variables: Elastomer composition, permeant composition, cross-link density, temperature.

Method: Permeation, sorption, thermal expansion, thermal conductivity, physical properties (modulus, tensile strength).

5 ADDENDUM

Although the preceding note was written some time ago, it is significant that there is little reason to modify the general conclusion as a result of recent developments. Some published work has reinforced several of the points made, and indicated the need for further investigations. The following comments are relevant.

Stannet [29] has reviewed some of the more general problems of polymer films and permeability, the effects of plasticization and the properties of composite films. Frisch [30] has given a mathematical treatment of flow in inhomogeneous membranes, and makes the point that it may be difficult to distinguish between convective flow and diffusional flow, a distinction we have not made earlier.

Frisch [31] also developed equations for diffusion through linear laminated media, and Mehta et al. [32] developed a treatment for transport through composite films (glass ribbon in cellulose acetate), which indicates that tortuosity can load to reduced permeability, and could be perhaps gainfully used.

Flow through membranes has continued to excite much work. Greenlaw [33] has developed models for liquid flow for single fluids and binary mixtures through membrances and accounted for the effect of pressure on either side. Paul [34] has reviewed his theories, which continue to interest other workers [35] as they are extended [36].

It has been shown that diffusion of gases through rubber impregnated textiles does not necessarily follow an Arrhenius temperature dependence [37], and that compounding (cure system, filler) is important in determining the permeability of an NBR rubber system [38].

In short, the technological problem of permeability of a composite elastomeric fabric has still not been addressed in the literature. Work done at NRL [39] has investigated suitable experimental configurations, and demonstrated some of the considerations raised in this report.

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