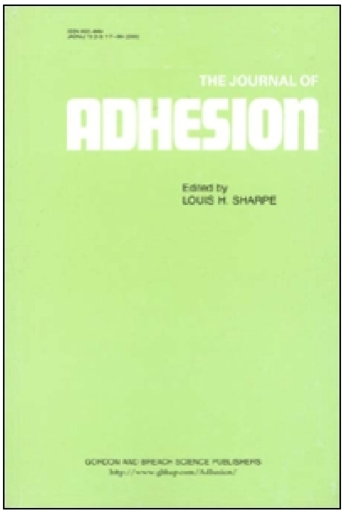

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Osmosis and the Kinetics of Percolation of Petroleum Products Through an Epoxy Adhesive

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Osmosis and the Kinetics of Percolation of Petroleum Products Through an Epoxy Adhesive†

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A moiré optical interference method has been used to investigate the dimensional changes that occur in an FM1000 epoxy adhesive joint between a microscope cover slip and a block of glass during exposure to dried 99% *n*-octane, to kerosene and, simultaneously, to kerosene plus water. The immediate response to *n*-octane uptake is shrinkage around the edge of the joint. Within 2 hours at 60°C the octane has permeated right across the joint to give a distribution of moiré fringe loops indicative of local swellings. The activation energy deduced from the temperature dependence of this permeation time is 14 kcal mol^{-1}. Examination in a microscope reveals the presence of clusters of particles beneath each region of local swelling and, between crossed polars, strong photoelastic contrast adjacent to each particle. These observations are similar to those for exposure of the same joint to commercial kerosene and indicate that the photoelastic contrast in both cases should be attributed to the interaction of octane with the particles. The same experiment has been repeated for a specimen immersed half in water and half in kerosene; although swelling (and no shrinkage) occurs all around the edge, there is no significant change in the time required for the appearance of moiré fringe loops across the specimen.

KEY WORDS Osmosis, octane uptake, kerosene uptake, water uptake, simultaneous uptake of kerosene and water.

1 INTRODUCTION

The widespread use of epoxy-based materials, adhesives and fibre reinforced composites, to fabricate storage tanks for petroleum products has focussed

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attention on the mechanisms and consequences of leakages, to the outside, of the fluid stored inside. The present work reports on the kinetics of permeation of octane, of kerosene and, simultaneously, of kerosene plus water through a proprietory epoxy resin. As marker for the extent to which seepage of fluid occurs at different temperatures, use is made of the deformation adjacent to osmotic pressure filled pockets arising from dissolution of solutes present in the resin as impurity inclusions.

2 EXPERIMENTAL

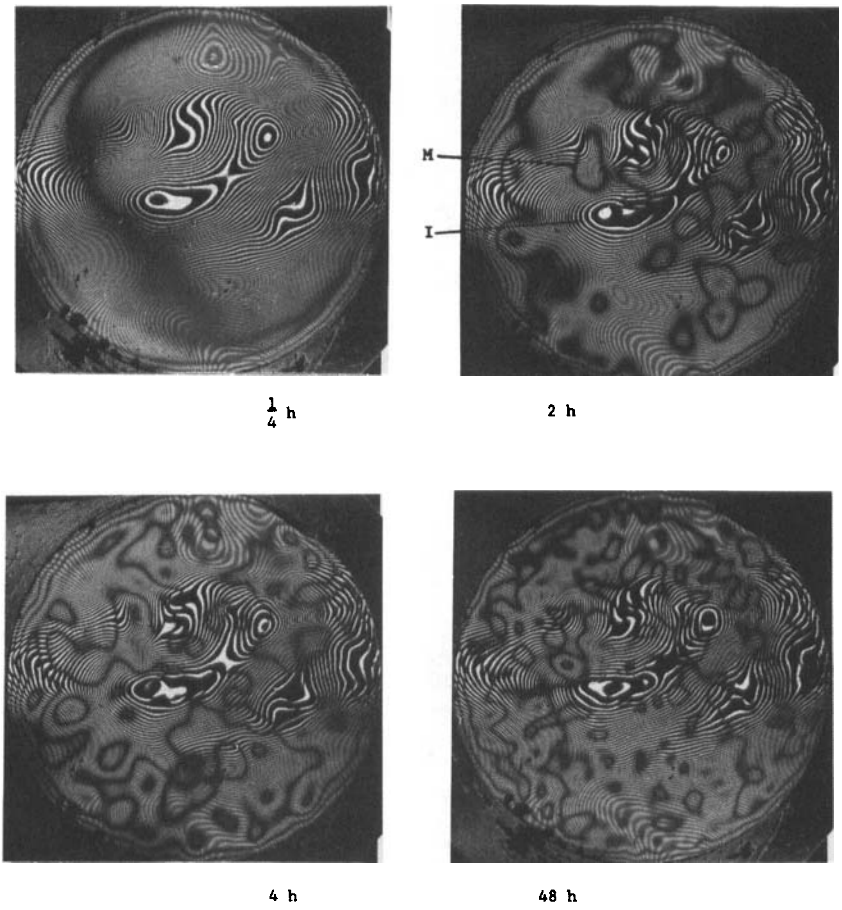
A novel moiré optical interference method, originally developed by the authors to measure the swelling normal to the plane of a simple butt joint during water uptake at the joint edge,[1] was later used to study deformations of opposite sense, *i.e.* shrinkage, during uptake of kerosene.[2] The method employs a thin glass cover slip as one adherend; local deformations in the adhesive film are faithfully transmitted to the cover slip and changes in thickness of the gap between the latter and an adjacent optical flat are exploited by way of optical interference in order to map the deformations. In addition to detection of the overall level of swelling at the joint edge it is possible to identify localised swellings around internal pressure pockets arising from osmosis[3] and it is this observation that is used in the present work to determine how far the diffusing solvent has penetrated. The joints are made between a coverslip and a microscope slide using American Cyanamid's FM1000 film adhesive, a modified epoxy.

Since kerosene and water produce dimensional changes of opposite sign, it is of some interest to enquire about the combined effect of both diffusing species. An experiment has been designed to answer this question.

Drying of the octane for the present experiments was carried out for 100 hours in air at less than atmospheric pressure in a desiccator which contained phosphorous pentoxide.

3 RESULTS AND DISCUSSION

Figure 1 shows a pattern of interference fringes photographed at four different times of immersion of a joint in dried *n*-octane at 60°C. Each photograph has been superimposed on a photograph of the same interference pattern, taken at zero time of immersion, in order that any displacement of fringes, cause by changes in thickness of the resin beneath the cover slip, may generate moiré fringes and hence more easily reveal the nature of the thickness changes. In Figure 1(b), the interference fringes are labelled "I" and the moiré fringes "M". It is evident that a system of circumferential moiré fringes develops around the edge of the joint, and that isolated loops of moiré fringes form throughout the joint. By clamping, in order to close the joint, it was confirmed that the circumferential fringes are due to resin shrinkage normal to the joint, and



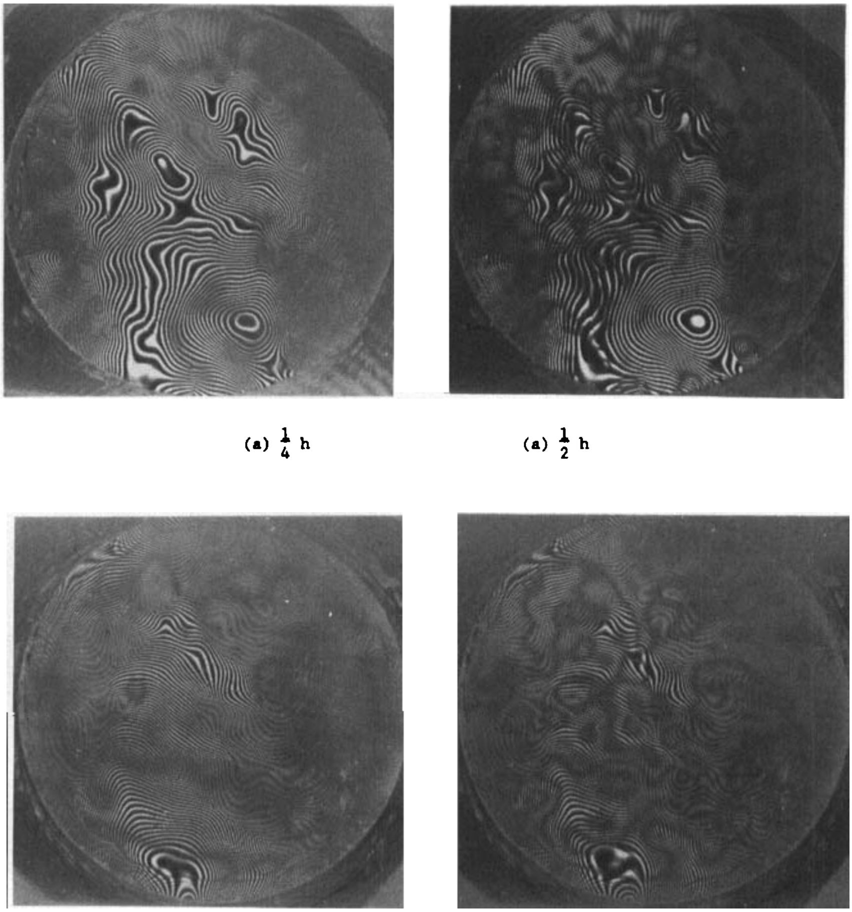
$\frac{1}{4}$ h 2 h

4 h 48 h

FIGURE 1 Optical interference fringes (I) and moiré fringes (M) for a specimen undergoing uptake of dried *n*-octaine at 60°C. The numbers indicate time of uptake in hours.

established that the loops are due to resin swelling. Thus, from $\frac{1}{4}$ h to 2 h onwards the cover slip adopts a contorted shape consisting of saucer-shaped deformation to form a lip around its edge, plus many isolated dome-shaped distortions all across its area.

When examined in a polarising microscope, each region of localised resin swelling was found to contain lobes of birefringent contrast around *internal* impurity inclusions. The sign of the birefringence adjacent to each inclusion corresponds to that expected to result from internal pressure generated at the inclusion. As in the case of pressure pockets following water uptake, a likely mechanism whereby diffused octane generates pressure at an impurity inclusion is osmosis. Published data on measured osmotic pressures of solutions in organic solvents were compiled in several editions of Landolt–Bornstein[4] early this



(a) $\frac{1}{4}$ h

(a) $\frac{1}{2}$ h

(b) 71 h

(b) 167 h

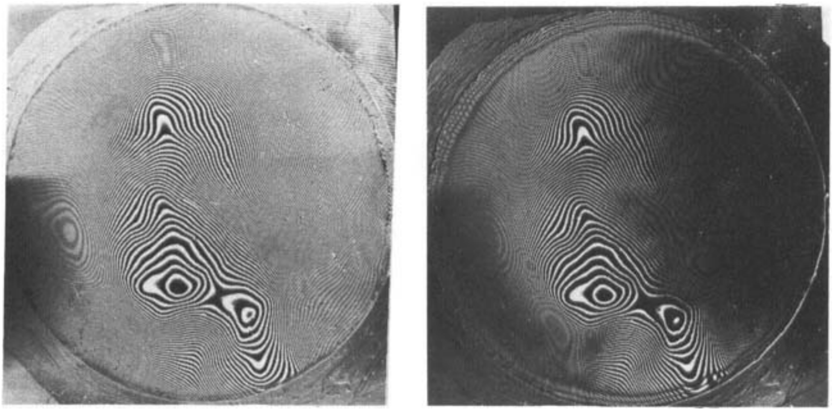
FIGURE 2 Same as Figure 1 for immersion in *n*-octane at (a) 80°C, and (b) 44°C.

century, and include the following:

100 bars for 14.1% nitrocellulose in acetone at 25°C
105 bars for 24% calcium chloride in alcohol at 40°C

100 bars (10 MNm^{-2}) is of the order of the yield strength of hot epoxy resin saturated with *n*-octane, and would certainly be large enough to account for the observed localised deformations. If the osmosis hypothesis is correct the addition of inorganic salts to the octane should lengthen the time of immersion at which localised swelling appears.

Figure 2(a) and (b) shows interference patterns and moiré fringes for joints immersed in octane at 80°C and 44°C respectively. Figure 3 shows a similar pattern and fringes for room temperature immersion; in this case, no evidence of closed loops of moiré fringe was found during immersion times up to 672 h.



48 h

672 h

FIGURE 3 Same as Figure 1 for room temperature immersion in *n*-octane.

The cover slips used as flexible adherend in each of the joints photographed in Figures 1, 2 and 3 were nominally 2 cm in diameter. If the octane permeation rate is assumed to be uniform, the time at which moiré loops appear in the middle of a joint, that is, at distance 1 cm from the edge, may be used to estimate that rate. Table I lists the permeation rates determined in this way at the four different temperatures. The slope of the rate *versus* $1/T$ relationship sketched in Figure 4 is -7×10^3 K, from this it is deduced that the activation energy for permeation of this particular epoxy by *n*-octane is

$$\begin{aligned} Q &= 2\,(\text{cal} \cdot \text{mol}^{-1}\text{K}^{-1}) \times 7 \times 10^3\,(\text{K}) \\ &= 14\,\text{kcal mole}^{-1} \end{aligned}$$

If we take, as trial mechanism for the permeation process, Fickean diffusion then the diffusion coefficient D is given by the approximate formula

$$D = x^2/t$$

TABLE I

T (°C)	$1/T$ (K^{-1})	Permeation rate (cmh^{-1})	Permeation rate (ms^{-1})
80	2.8×10^{-3}	$\frac{1\,(\text{cm})}{1/4\,(\text{h})} = 4$	1.1×10^{-5}
60	3.0×10^{-3}	$\frac{1\,(\text{cm})}{2\,(\text{h})} = 0.5$	1.4×10^{-6}
44	3.2×10^{-3}	$\frac{1\,(\text{cm})}{54\,(\text{h})} = 0.02$	5.2×10^{-8}
20	3.4×10^{-3}	$\frac{1\,(\text{cm})}{>672\,(\text{h})} = <0.0015$	4.2×10^{-9}

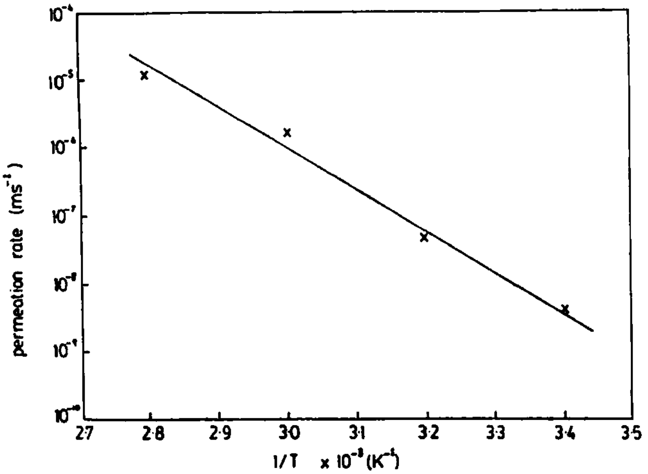


FIGURE 4 *n*-octane permeation rate *versus* reciprocal temperature.

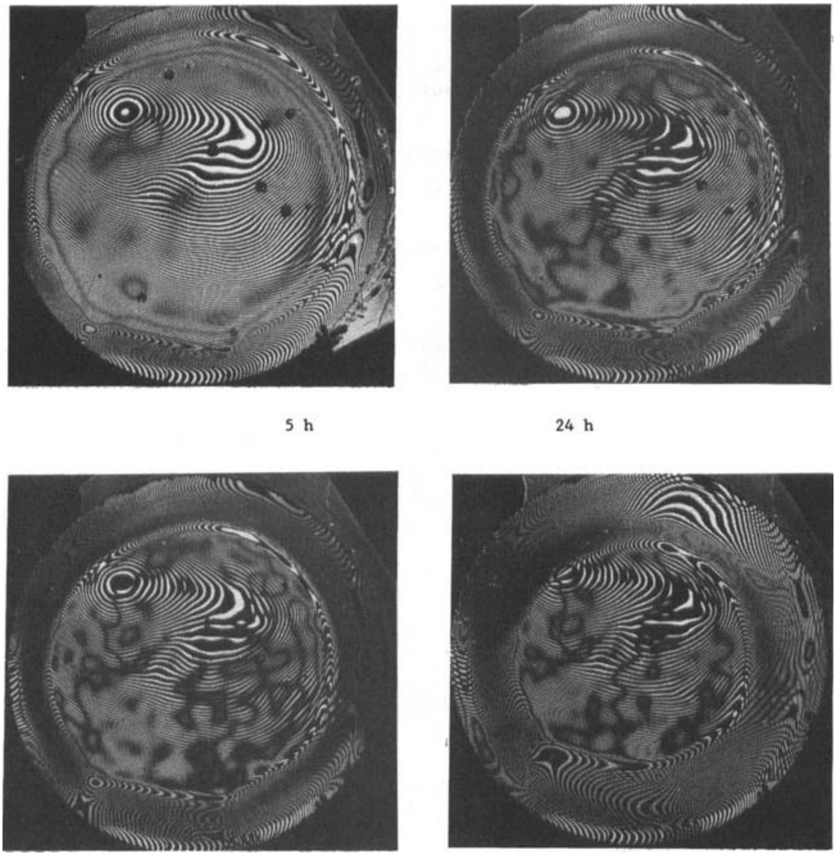
where x is the diffusion distance in time t. Substituting $x = 1$ cm and $t = 900$ s, we find $D = 10^{-3}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ at 80°C. This is about two orders of magnitude larger than the diffusion coefficient for water in the same resin at the same temperature.

A better model for permeation of linear chain hydrocarbons might be the mechanism that de Gennes[5] calls reptation. In this mechanism the molecule is assumed to migrate by way of thermally activated advance of random segments which then drag forward the intervening lengths of molecule—a process not unlike the motion of a side-winder snake. In any event, it is to be concluded that *n*-octane is able to pass through epoxy resin at remarkably high rates.

Finally, Figure 5 shows a sequence of photographs of the interference pattern and moiré fringes obtained during 60°C immersion of a joint, half in water and half in kerosene; the joint is held vertical and the water/kerosene interface is horizontal in the photographs, approximately coinciding with the horizontal diameter. For comparison, Figure 6 shows a corresponding pattern and fringes for a joint immersed in commercial kerosene also at 60°C. In both cases, Figures 5 and 6, the time taken for moiré loops to appear at the center of the joint is about the same as that for the joint immersed in dried *n*-octane at 60°C, Figure 1. The main difference between Figures 5 and 6 is that the circumferential moiré fringes for the water plus octane uptake case, Figure 5, correspond to swelling—not shrinkage.

4 CONCLUSIONS AND GENERAL DISCUSSION

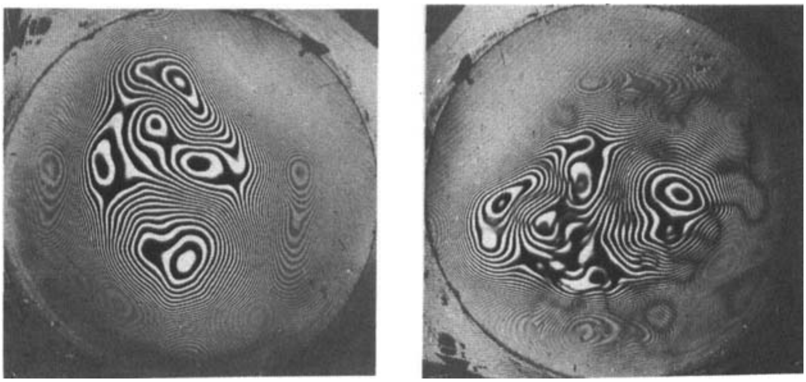
1. The immediate response of FM 1000 epoxy adhesive, to absorption of each of dried *n*-octane and commercial kerosene, is shrinkage amounting to three or four half-wavelengths (10 μm) in a sample thickness of, say, 200 μm. This



5 h 24 h

32 h 71 h

FIGURE 5 Same as Figure 1 for immersion of the lower half of the specimen in water and the upper half in kerosene. Temperature 60°C.



2 h 8 h

FIGURE 6 Same as Figure 1 for immersion in kerosene at 61°C.

shrinkage we attribute to leaching out of low molecular weight material. The consequent loss in weight of the resin counterveils the gain in weight due to the presence of absorbed octane (of kerosene in the case of kerosene uptake) and explains why very little net change in weight is associated with exposure of resins to petroleum products.

2. That *n*-octane, and probably other fractions in the case of kerosene, permeates the resin at remarkably fast rates (5 millimeters per hour at 60°C falling to a micrometer or so per hour at room temperature) has been demonstrated by direct observation and measurement of the displacement field generated by osmosis at solutes located at large distances (~1 centimeter) from the free surface.

3. The activation energy for permeation of *n*-octane is ~ 14 kcal mole^{-1}.

4. Assuming Fickean behavior, the diffusion coefficient for uptake of *n*-octane is $\sim 10^{-3}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ at 80°C falling to $< 4 \times 10^{-7}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ at room temperature.

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