A Method for Determining the Permeability and Solubility of Sulfur in Poly(dimethylsiloxane) (RTV)

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Synopsis

A method has been devised whereby the S_8 permeability and solubility in silicon resin are determined by observing the reaction between sulfur vapors and silver particles within the polymer. The particles ($\sim$10 μm diameter), which may vary between 0.1 and 100 μm in diameter, are dispersed in the polymer at a concentration up to 20% within a glass cylinder (also an aluminum container). The polymer is cured according to procedure and exposed to S_8 saturated vapors at various temperatures (55°–125°C), leaving one end of the cylinder open. The Ag particles are a perfect *sink* for sulfur, which is consumed as soon as it reaches the reaction boundary that separates the reacted and unreacted Ag particles. Consequently, a distinct black region containing Ag_2S product is left behind as the boundary advances. The line displacement, measured at time intervals for the several temperatures, is used to calculate the gas permeability in the polymer as a function of temperature on the basis of a mass transport model developed from diffusion theory. The S_8 solubility in the polymer is calculated from the permeability and diffusivity. The latter is determined independently by measuring the time that the Ag_2S reaction is delayed when a layer of plain polymer separates a silver surface and the sulfur environment.

INTRODUCTION

The rates at which gases permeate polymers, elastomers, and glasses are readily measured since films of these materials can be easily made. The instruments required for such measurements, however, are usually expensive and sophisticated and cannot be used for gas systems that are corrosive and attack the vital parts of these instruments.

The transport of a gas through a film involves the adsorption of the gas on the film surface at the inlet side, its solution into the material, the diffusion of the gas through the thickness of the films, and, finally, the dissolution and desorption of the gas on the outlet side of the film. At the outlet side of the film one can have a metal surface in contact with it so that a chemical reaction can take place between the gas and the metal. The thickness of the reacted films (or the x-ray intensity of the reacted gas) as a function of time is used to calculate the permeation rate and the diffusion coefficient. To measure the diffusion coefficient in this manner, we must assume that the diffusion process controls the rate at which the permeation process goes on; therefore the rates of adsorption, solution, and reaction must be relatively fast. Another requirement is that the gas concentration be low enough so that interaction between gas modules is negligible. In general, the assumptions made here are justified, and the stated requirement is met.

In practice, the permeation measurement is accomplished by pumping out both sides of the film and then introducing the permeating gas on one side at atmospheric pressure or at some saturated vapor pressure that is characteristic

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of the gas system. The volume of the gas that reaches the opposite side is then measured by pressure gauges or radiation counters (when isotope tracers are used) as a function of time. The equipment is arranged so that the amount of gas permeating the film is maintained sufficiently low that the pressure drop at the inlet side is negligible and the pressure in the other side is very small. Under these conditions, the concentrations of the gas on the inlet and outlet surfaces of the film are constant and equal to C and zero, respectively. If the gas is allowed to react with a metal surface in contact with the outlet side (for which the process is diffusion controlled), the same condition of zero pressure is achieved at the outlet surface. If the metal surface is that of metal particles dispersed in the matrix, the same situation would exist in each particle interface while the diffusion of the gas through the matrix would control the amount of reacted metal. This is, in fact, an alternative way to the classical approach and is the subject of this paper.

The method is based on the use of metal powder dispersed in the polymer or elastomer and by observing the rate at which the metal reaction proceeds. The reaction progress is observable if the metal selected forms a dark compound with the gas so that it is visible and distinguishable from the unreacted region. To be able to observe the phenomenon, however, the polymer or elastomer must be contained in the glass tubes with one and open during exposure to the gas. Again, the assumption here is that diffusion is the rate-limiting step, as the metal particles react with the gas instantaneously. In general, this requirement is satisfied Because of the fast reaction (in comparison to diffusion), the gas is now allowed to diffuse past a metal particle until it is completely consumed, hence forming a definite reaction line which propagates with time.
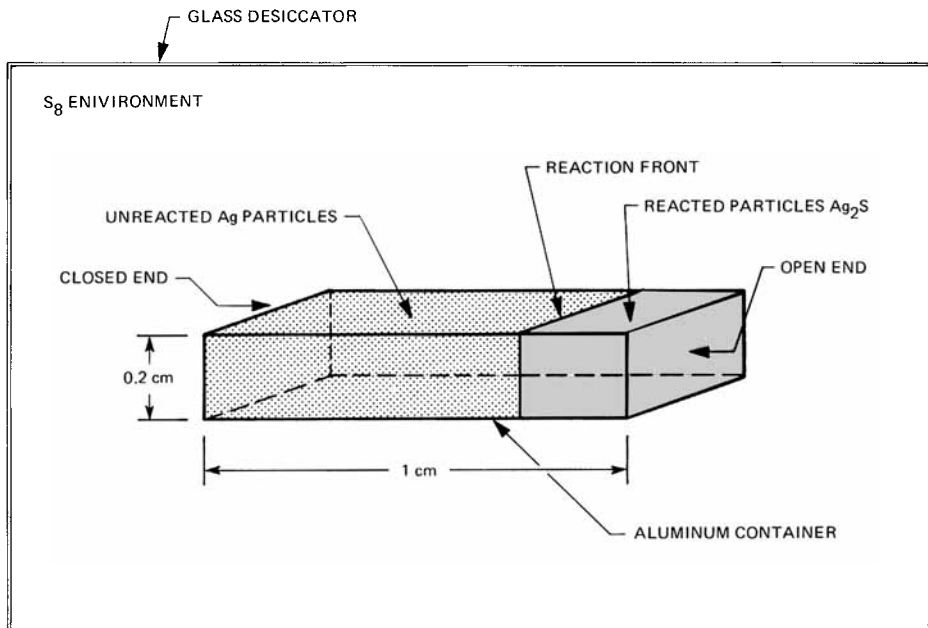

Fig. 1. Test setup for determining the S_8 diffusivity–solubility product DC in silicon rubber.

The other approaches (along the same line) are those concerned with diffusion-controlled precipitation in glasses. When the rate at which a substance precipitates within a glass (polymer or other materials) is controlled by diffusion and the precipitate growth rate can be measured, the diffusion coefficient of the substance can be calculated on the basis of the rate at which an isolated spherical particle of zero initial radius grows by diffusion.[4,5]

In the present work with the Ag–S–polymer system, a model has been developed (see Appendix) on the basis of bulk diffusion and moving reaction boundary[6] which enables one to calculate the diffusion properties of the sulfur through the polymer using the rate at which the reaction line moves, the compound stoichiometry, and the metal concentration in the matrix.
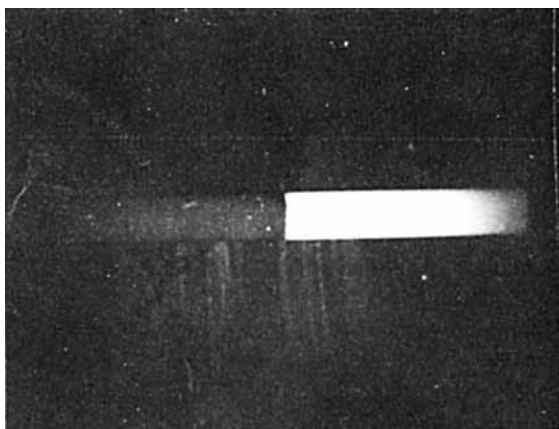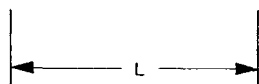

(a)
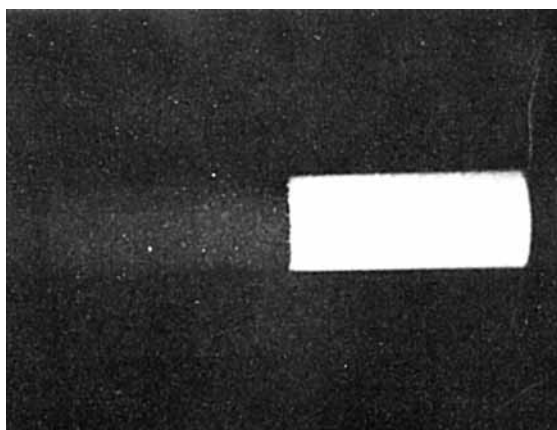
(b)

Fig. 2. Diffusion in glass tube: (a) 10% Ag concentration in polymer; (b) 20% Ag.

While other methods may be available for solubility and diffusion measurements of gases in polymers,[7] their applicability to sulfur vapors (in equilibrium with the solid) at ambient temperature is not generally suitable, mainly because of the low vapor pressure ($\sim 10^{-6}$ torr).
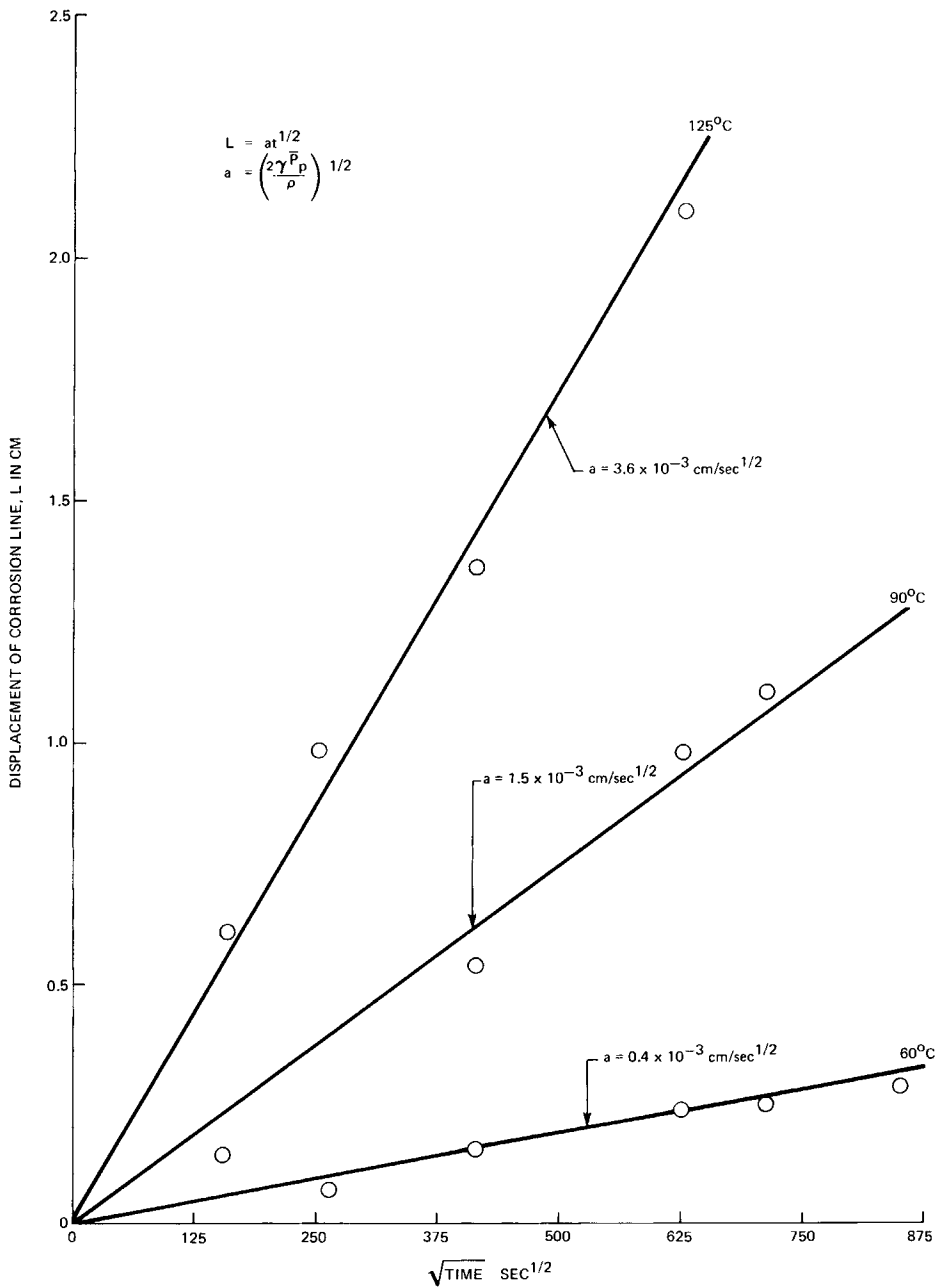
$$L = at^{1/2}$$
$$a = \left(\frac{2\gamma \overline{P}_p}{\rho}\right)^{1/2}$$

Fig. 3. Corrosion line displacement vs $\sqrt{\text{time}}$ for $\gamma = 1$.

APPROACH AND RESULTS

Determination of Permeability

Silver particles having a radius of $\sim$10 μm were dispersed in RTV, a polymer of the poly(dimethylsiloxane) type, at a fractional weight $\alpha = 0.20$.   The polymer
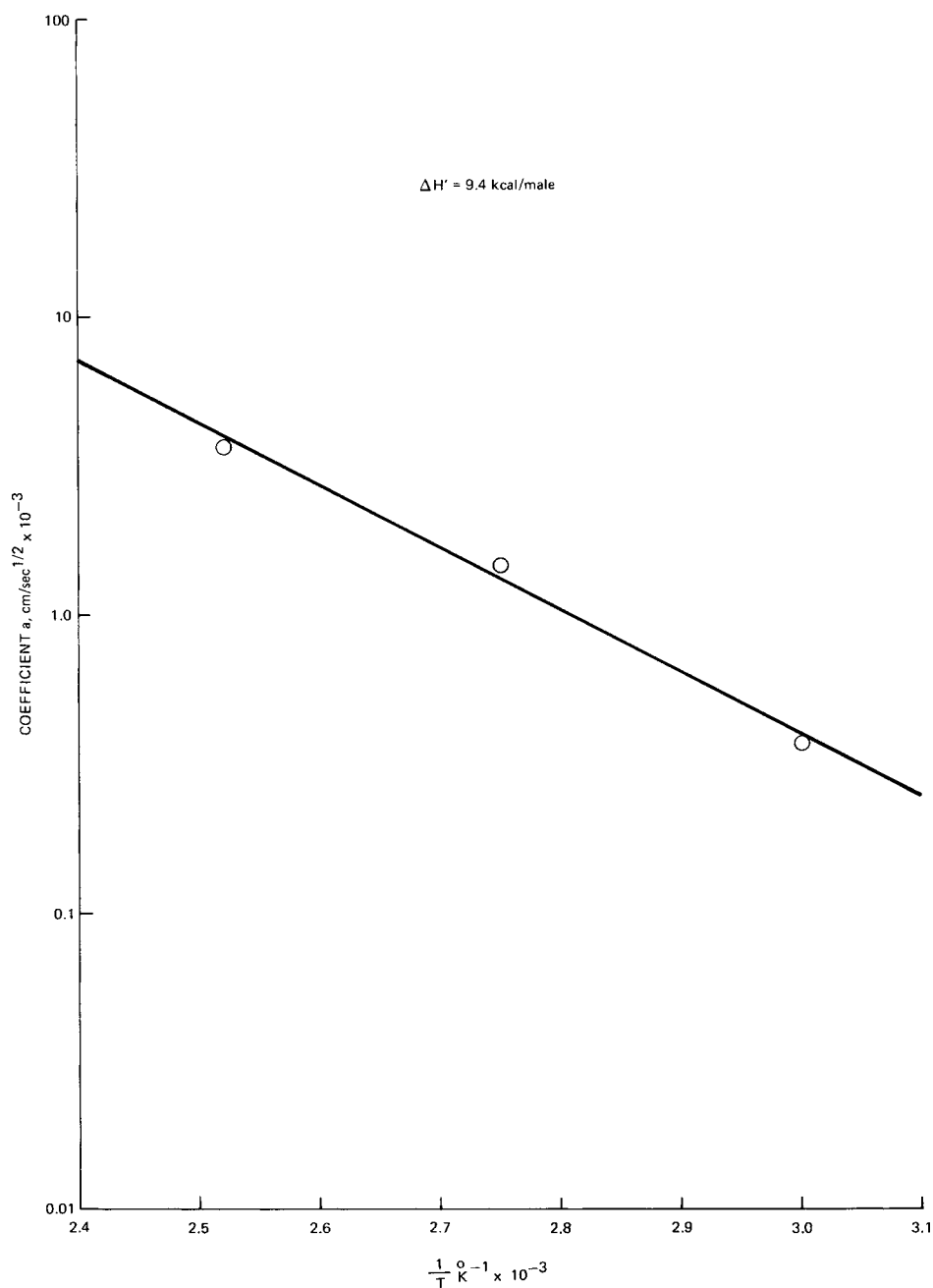

Fig. 4. Activation energy for S_8 diffusion through silicon rubber, $\gamma = 1$.

was subsequently cured in aluminum containers of parallelepiped shape which had the small end open. The samples were exposed to saturated S_8 at the given temperatures for various times. Figure 1 shows a diagram of the sample within the test environment. The silver particles (20% of the polymer weight) represent only 3% of the volume and have an average separation of $\sim$30 μm.

As the S_8 diffuses through the polymer, the Ag particles act as a *sink* for the sulfur so that (within a narrow corrosion region) a reaction front line is produced. The line velocity of propagation depends on the concentration of Ag particles with respect to the polymer (or concentration of combined sulfur), sulfur diffusivity and solubility, activation, energy, time, and temperature. The distance
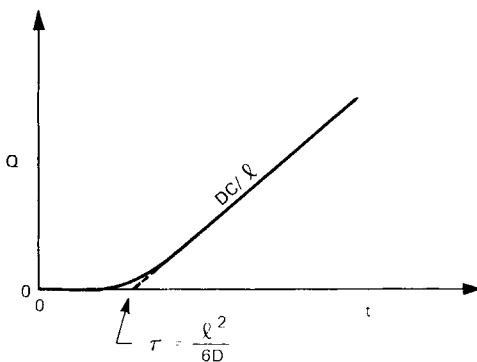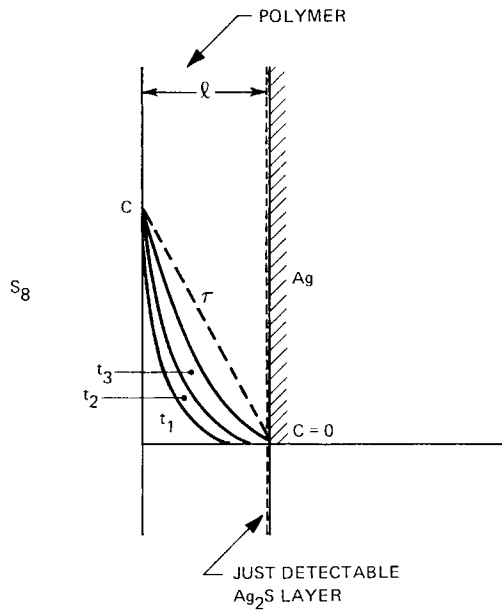
$$Q = \frac{CD}{\ell}\left(t - \frac{\ell^2}{6D}\right)$$

Fig. 5. Determination of D in terms of delay time τ.

L traveled by the corrosion front line is expressed by the following equation (see Appendix):

$$L = \left(\frac{2\gamma C_0 D_0 t}{\rho R}\right)^{1/2} \exp \frac{\Delta H}{2R}\left(\frac{1}{T_0} - \frac{1}{T}\right) \tag{1}$$

or

$$L = \left(\frac{2\gamma \bar{p}_p t}{\rho R}\right)^{1/2}$$

and the propagation rate is

$$\frac{dL}{dt} = \frac{1}{2}\left(\frac{2\gamma C_0 D_0}{\rho R t}\right)^{1/2} \exp\frac{\Delta H_p}{2R}\left(\frac{1}{T_0} - \frac{1}{T}\right) \tag{2}$$

where p = vapor pressure, cm Hg; $H_p = H_d + H_s$, activation energy of permeation; ΔH_p = activation energy of diffusion for S_8; ΔH_S = heat of solution for S_8; ρ_R = density of reacted sulfur, 0.03 g/cm^3 of polymer; D_0 = diffusivity of S_8 at 125°C, cm^2/sec; C_0 = solubility of S_8 at 125°C, g/cm^3; R = gas constant, cal/mole-°K; T_0 = 398°K (125°C); γ = ratio of S_8 ingress area to container cross section; and $\bar{p} = \bar{p}_0 \exp \Delta H_p/R(1/T_0 - 1/T)$.

Two sets of experiments were conducted to verify eq. (1). One experiment was run at 55°, 85°, and 125°C with the aluminum container (Fig. 1), while the other was performed in a cylindrical glass tube at 60°, 90°, and 125°C (Fig. 2). The data obtained from the latter is shown in Figure 3. The results fit the propagation time dependence expressed by eq. (1) and therefore verify the validity of the assumption that the process is diffusion controlled. For the three temperatures, the distance L traveled by the corrosion line fits

$$L = a t^{1/2} \tag{3}$$

where a equals 3.6×10^{-3}, 1.5×10^{-3}, and 0.4×10^{-3} cm/sec$^{1/2}$ at 125°, 90°, and 60°C, respectively. At any given time, L is proportioned to a, therefore a plot of ln a versus the reciprocal of the absolute temperature yields an activation
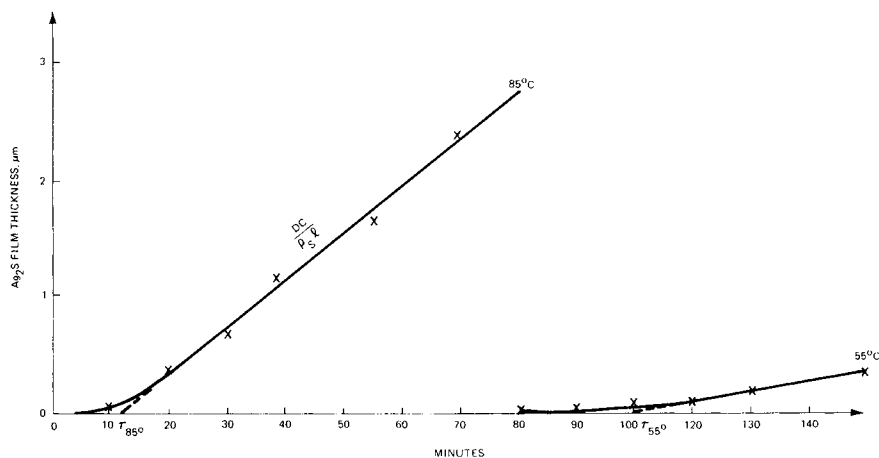

Fig. 6. Thickness of reacted layer vs time and delay time intercept τ.

energy of ΔH_p = 9.4 kcal/mole (see Fig. 4).   Using eq. (1), the value of the product $C_0 D_0$ is obtained at 125°C:

$$D_0 C_0 = \frac{\rho_R L^2}{2\gamma t} = P_0 P_0 \qquad (4)$$

where $\overline{P}_0$ = permeability of S_8 at 125°C, g-cm/sec-cm^2-cm Hg; and P_0 = vapor pressure of S_8 at 125°C, cm Hg.   Equation (4) yields $\overline{P}_0 p_0 = 1.55 \times 10^{-7}$ g/cm-sec,
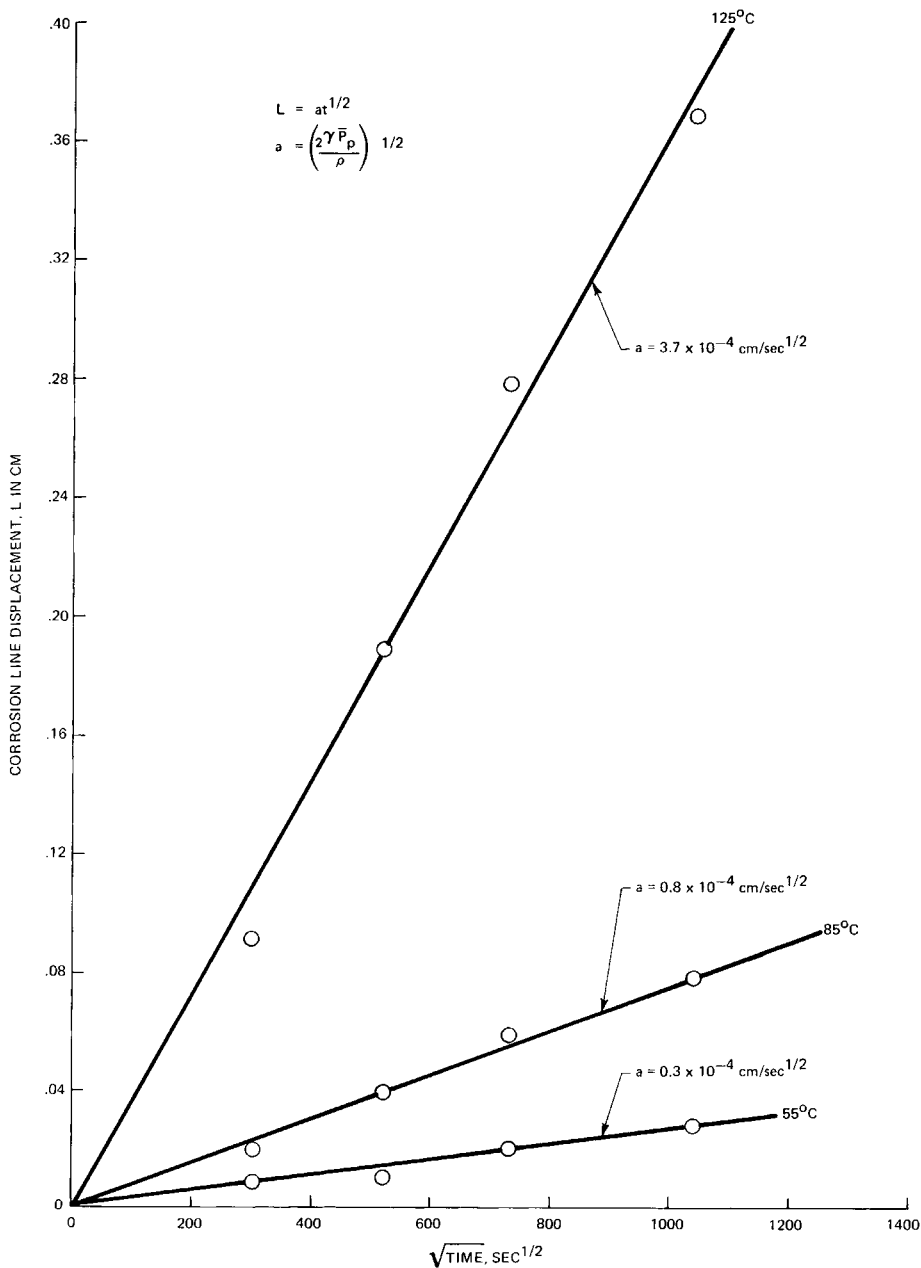

Fig. 7. Corrosion line displacement vs $\sqrt{\text{time}}$ for = 3×10^{-3}.

from which $\overline{P}_0 = 3 \times 10^{-4}$ g-cm/sec-cm^2-cm Hg based on the value of $P_0 = 5.4 \times 10^{-4}$ cm Hg.

Determination of S$_8$ Diffusivity

On the basis of Ag–S reaction kinetics,[8] Ag$_2$S is formed at a relatively fast rate that is linearly related to the S$_8$ vapor pressure for sulfide thicknesses of the
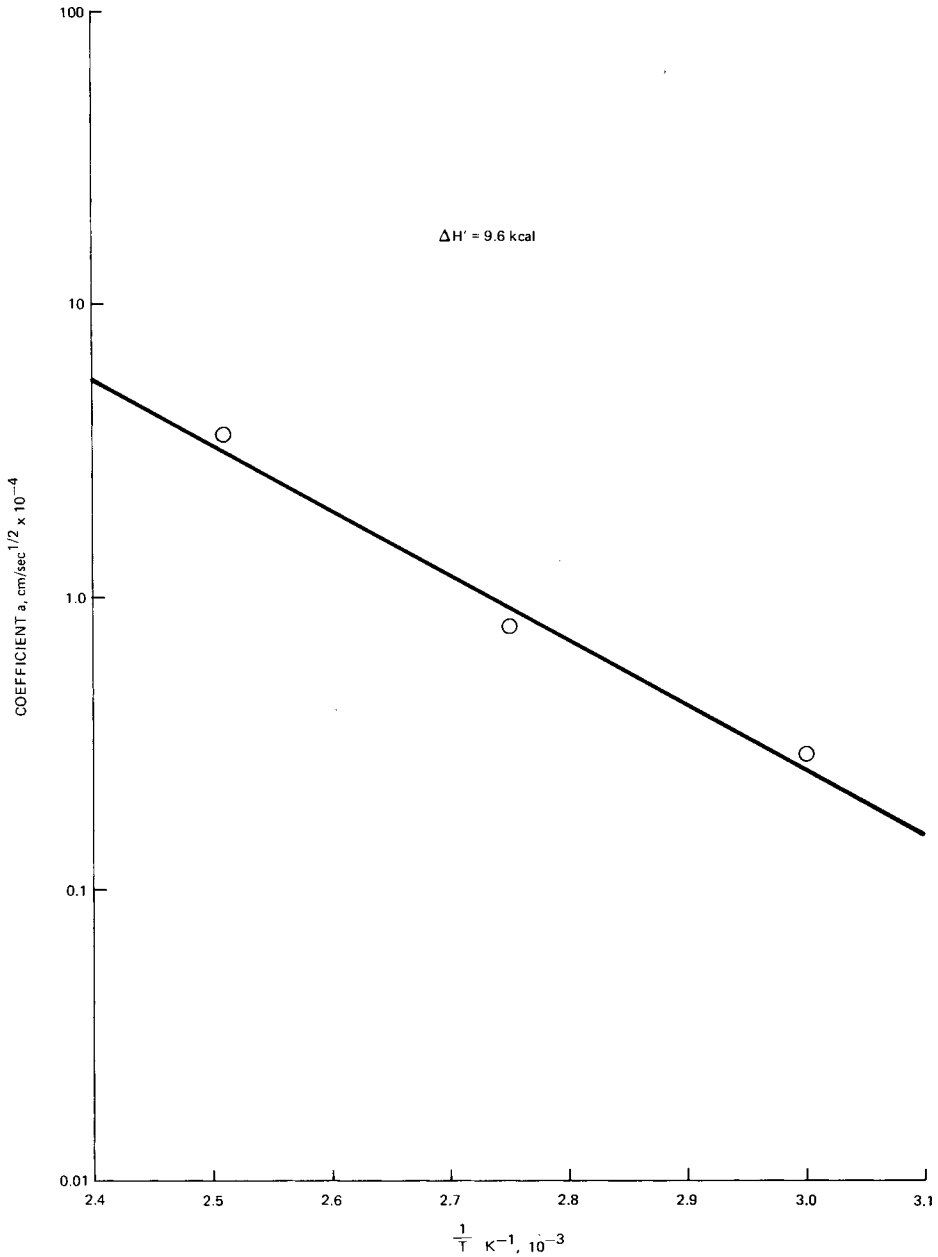

Fig. 8. Activation energy for S$_8$ through silicon rubber, $\gamma = 3 \times 10^{-3}$.

order of 1 μm,[8] indicating that the reaction rate is not controlled by Ag diffusion through Ag$_2$S. If the silver surface is coated with the polymer, therefore, the sulfur diffusivity through the polymer can be determined in terms of the delay time τ, using the steady-state solution to the diffusion equation for thin films[6]:

$$r = \frac{DC}{l\rho_{Ag_2S}} \left(t - \frac{l^2}{6D} \right) \tag{5}$$

where r = thickness of Ag film reacted after time t, sec; D = diffusion coefficient, cm^2/sec; C = concentration of S$_8$ in RTV, g/cm^3; l = thickness of polymer film, cm; and ρ_{Ag_2S} = density of Ag$_2$S, g/cm^3.

When the Ag$_2$S sulfur has just permeated the polymer film and has begun to react with the silver surface, a time τ will have elapsed at which r is practically zero (Fig. 5). Therefore,

$$\tau = \frac{l^2}{6D} \tag{6}$$

For a polymer film 0.15 cm thick covering the silver, the value of τ was −750 sec at 85°C. Using eq. (6), the diffusivity $D_{850} = 5.5 \times 10^{-6}$ cm^2/sec was calculated. The experiment was repeated at 55°C. The value of $D_{550} = 6.2 \times 10^{-7}$ cm^2/sec was calculated on the basis of a delay time $\tau \simeq 6100$ sec (Fig. 6). The activation energy of diffusion $\Delta H_D = 0.77$ eV, or 18 kcal/mole, was determined from the diffusivities at the two temperatures in Figure 6. From the known activation energies of diffusion and permeation, the heat of solution $\Delta H_S = 8.6$ kcal/mole was calculated. Also, on the basis of the activation energy of diffusion, the coefficient $D_{125°} = D_0 = 2 \times 10^{-4}$ cm^2/sec was obtained. Using this diffusivity value and the product $C_0D_0 = 3.1 \times 10^{-7}$ g/cm-sec determined earlier, the value of C_0 is obtained from $C_0D_0/D_0 = 1.6 \times 10^{-3}$ g/cm^3, which is in good agreement
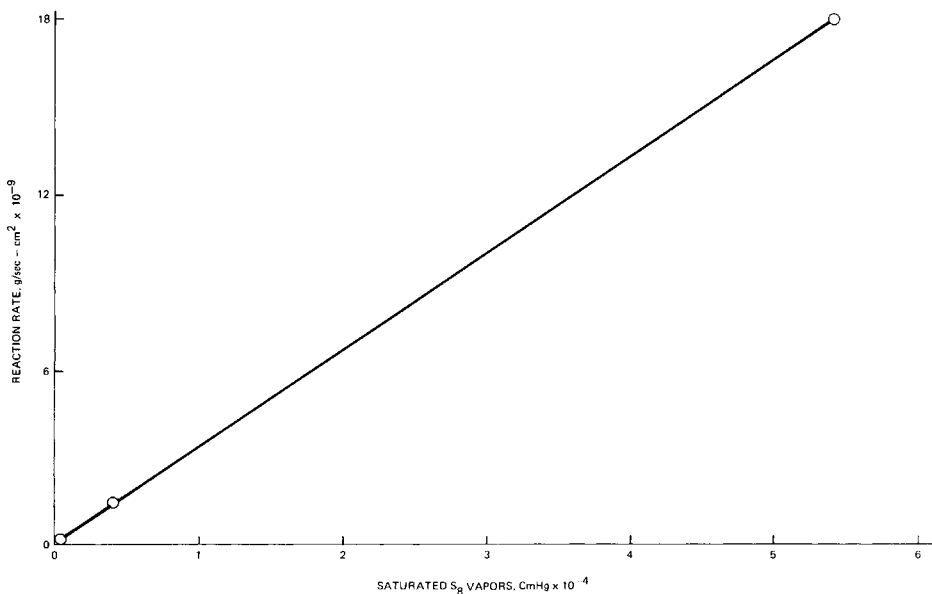

Fig. 9. Reaction rate vs saturated S$_8$ vapors.

with the value determined by Berry and Susko[9] by an independent method. The diffusivity D, the specific solubility $S = C/p$, and the permeability $P = DS$ at other temperatures are calculated from

$$D = D_0 \exp \frac{\Delta H_D}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \qquad (7)$$

$$S = S_0 \exp \frac{\Delta H_S}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \qquad (8)$$

$$P = P_0 \exp \frac{\Delta H_p}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \qquad (9)$$

The experiment with the aluminum container was conducted under the conditions already described, with the exception that instead of leaving the entire side open, only a circular opening of area 3×10^{-4} cm^2 ($\gamma = 3 \times 10^{-3}$) was made. The results are shown in Figure 7, which verify eq. (1) for $\gamma \ll 1$. The rates are smaller by a factor of $\sqrt{\gamma}$ as predicted by the model. The activation energy of permeation ΔH_p determined from the data is ~ 9.6 kcal/mole (Fig. 8), which is very close to that determined from the previous experiment for which $\gamma = 1$ (Fig. 4). The specific solubility $\overline{S}$, expressed in g of sulfur per cm^3 of polymer per cm Hg, is

$$\overline{S} = \frac{C}{P}$$

which is the ratio of $\overline{P}/D$.

Table I shows the permeation parameters determined in the two experiments based on the rates of permeation at the various temperatures. The results show that these parameters are obtainable with good reproductibility by different approaches.

Determination of Corrosion Interface Width W

A previous study[8] has shown that the kinetics of Ag films with S$_8$ vapors can be expressed as

$$\dot{r} = \frac{\beta P_0}{\rho_{\text{Ag2S}}} \qquad (11)$$

where $\beta = 3 \times 10^{-3}$ g/cm-sec-cm Hg.[9] Equation (11) expresses the rate at which the silver particles are consumed for a given sulfur concentration P_0. The rate at which the reaction line advances through the polymer is $\dot{L}$ as expressed by eq. (2) above. The ratio $r_0/\dot{r} = \Delta t$ represents the time required to consume a silver particle, which is relatively short, during which the corrosion line moves a distance $W = \dot{L} \Delta t$. Thus, the corrosion linewidth can be expressed as

$$W = \left(\frac{\dot{L}}{\dot{r}} \right) r_0 \qquad (12)$$

where $r_0 = 10^{-3}$ cm, the initial radius of Ag particles. Substituting $\dot{L}$ from eq. (2) and $\dot{r}$ from eq. (11) into eq. (12), we obtain

$$W = \frac{\rho S r_0}{2 \beta P_0} \left(\frac{2 \gamma D_0 C_0}{\rho_R t} \right)^{1/2} \exp \frac{\Delta H_p}{2R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \qquad (13)$$

TABLE I
Permeation Results

Container	T, °C	γ	Activation energy, (kcal/mole)			$\bar{P}$, g-cm/ cm²-sec-cm Hg	D_2, cm²/ sec	$\bar{S}$, g/ cm²-sec	C, g/ cm²	$a = \dfrac{2\gamma \bar{P} P}{\rho_R}$
			ΔH_P	ΔH_D	ΔH_S					
Aluminum can	125	3×10^{-3}	9.6	18.0	-8.4	3.0×10^{-4}	1.05×10^{-4}	3.0	16×10^{-4}	3.7×10^{-3}
Aluminum can	85	3×10^{-3}	9.6	18.0	-8.4	0.5×10^{-4}	0.4×10^{-5}	9.3	4.3×10^{-4}	0.8×10^{-3}
Aluminum can	55	3×10^{-3}	9.6	18.0	-8.4	2.3×10^{-5}	0.8×10^{-6}	29	1.2×10^{-4}	0.3×10^{-3}
Glass tube		1	9.4	18.0	-9.6	2.4×10^{-4}	1.0×10^{-4}	2.9	15.8×10^{-4}	3.6×10^{-3}
Glass tube		1	9.4	18.0	-9.6	0.45×10^{-4}	1.15×10^{-5}	8.2	5.1×10^{-4}	1.5×10^{-3}
Glass tube		1	9.4	18.0	-9.6	2.2×10^{-5}	1.1×10^{-6}	25	1.5×10^{-4}	0.4×10^{-3}

Expressing eq. (13) in more convenient terms,

$$W = \frac{r_0}{2\beta} \left(\frac{2\gamma\rho S\overline{P}_0}{\alpha\delta P_0}\right)^{1/2} \cdot t^{1/2} \exp\frac{\Delta H_p}{2R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$ (14)

where δ = fractional weight of sulfur in Ag$_2$S; $\alpha = 0.20$ = fractional weight of Ag in the polymer; and ρ_S = density of Ag$_2$S, g/cm^3. For $\gamma = 1$ and $T = 125°$C, eq. (1) predicts that after one day the reaction has advanced 1 cm, while the reaction linewidth W is 8×10^{-3} cm (or 0.8% of the reaction distance) as determined by eq. (1). At room temperature, the linewidth is $\sim 10^{-3}$ cm, which is comparable to the particle size and only 0.1% of the 1-cm distance. Longer times and smaller γ and r_0 make W even smaller. Therefore, we can use Ag particle concentrations of $\leq 1\%$ and still obtain excellent line sharpness comparable to the radius of the particles. In any case, an accuracy of $100(r_0/L)\%$ is easily achieved with great latitude.

CONCLUSIONS

1. A method for determining the permeability and solubility of sulfur in cured silicon resin has been developed on the basis of the corrosion kinetics of Ag particles embedded in the polymer.

2. The method allows the determination of permeability, diffusivity, and solubility of sulfur in the polymer as a function of temperature within the experimental range.

3. The method has an accuracy of $\pm 100(r_0/L)\%$, that is $\sim 10^{-2}\%$ (r_0/L is usually $\sim 10^{-2}$).

4. It can be applied to other polymers utilizing the sulfur–silver system or any other system that does not alter the permeation properties of the polymer and produces a visible reaction line as it propagates.

Appendix

The differential equation to be solved is the diffusion equation

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$ (1A)

assuming the diffusion coefficient is not a function of concentration. A solution to eq. (1A), as given by Crank[7] and Barrer[6] for thin films with the boundaries

$$C = C_0 \text{ at } X = 0 \text{ for all } t$$

$$C = 0 \text{ at } X = L \text{ for all } t$$

$$C = 0 \text{ at } 0 < X < L \text{ for all } t$$

leads to the expression

$$Q = \frac{CD}{L}t - \frac{LC}{6} - \frac{2LC}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp -\frac{Dn^2\pi^2 t}{L^2}$$ (2A)

For particle size $L = 10^{-3}$ cm, the summation term becomes insignificant when $t \geq t$ sec; therefore,

$$Q = \frac{CD}{L}\left(t - \frac{L^2}{6D}\right)$$

where $L/6D$ is the delay time which is of the order of 10' sec for L equal to the particle diameter. Consequently, steady state is achieved in ≤ 1 sec, and eq. (2A) reduces to

$$Q = \frac{DC}{L}t$$ (3A)

where Q = amount of S_8, g/cm^2, reacted within L; C = concentration of S_8 within the reacted zone L, g/cm^3; L = thickness of reacted zone of polymer, cm; and t = time, sec.

If the ingress area A_i for the diffusant is made smaller than the cross-sectional area A of the tube containing the polymer, the diffusion flux will be reduced by the ratio $A_i/A = \gamma$ so that the amount Q of reacted sulfur in eq. (3A) becomes

$$Q = \gamma DCt/L$$

At steady state, the amount of sulfur transported and the amount reacted per unit time are equal under these conditions, an expression for L as a function of D, C, P, and t is derived:
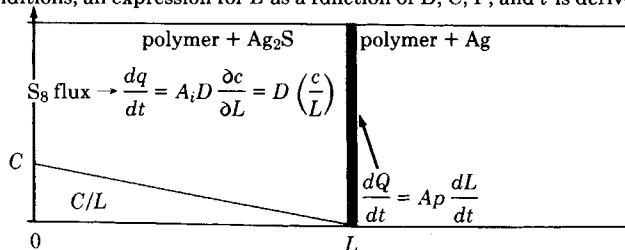
$$A p \frac{dL}{dt} = -A_i D \frac{\partial C}{\partial L} = A_i \frac{DC}{L} \tag{4A}$$

from which

$$\int_0^L L \, dL = \left(\frac{A_i}{A}\right) \int_0^t \frac{DC}{p} \, dt = \gamma \int_0^t \frac{DC}{p} \, dt; \qquad \frac{L^2}{2} = \frac{\gamma DC}{p}$$

and

$$L = \left(\frac{2\gamma DCt}{p}\right)^{1/2} \tag{5A}$$

where p = density of reacted sulfur with respect to the polymer, g/cm^3.

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