Fig. 2. Effect of degradation on sol/chain-density relation for tetramethylthiuram disulfide vulcanizate: (⊕) data from Fig. 1 for undegraded vulcanizate; (O) data for samples leached at 80° C. in 20% 2-ethylhexanoic acid in benzene before oxidation. Solid line is theory for "directed scission."

pending on the filler–rubber interaction. Two ways to observe a high solubility for a given extent of network degradation are known. Very readily oxidized samples often are oxidized inhomogeneously. This is frequently observed with peroxide gum vulcanizates, but is unlikely to be the explanation for the present results, since carbon blacks are antioxidants in peroxide vulcanizates. The second way to observe apparently high solubility is to use a partially degraded starting material. This is illustrated in Figure 2 for a TMTD vulcanizate; it has been described by Morton, Allen, and Gates.[8] A possible explanation of the curve for filled compositions may be, therefore, that there is extensive degradation of the polymer during milling in the presence of reinforcing fillers, previously unrecognized. All of the compositions used in the work reported here were prepared by a "low hysteresis" process,[9] which develops the maximum amount of covalent bonding to filler. This may have led to mechanical degradation, although no such effect has been detected in previous studies[10] of black masterbatch milling.

Although data for the gum vulcanizates appear to fit the predicted curve for "directed scission," independent evidence will be required before it can be concluded that non-random degradation occurs. The theoretical curve applies to a network which initially has no free ends and is without entanglements; neither of these conditions is true of the actual networks.

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Role of Diffusion in Antiozonant Action

INTRODUCTION

The cracking phenomenon exhibited by stretched rubbers exposed to ozone has been the subject of recent physical studies.[1] It was found that certain "antiozonants," namely, the N,N'-dialkyl-p-phenylenediamines, increased the critical stress necessary for crack growth to occur.[2]

It has been suggested by Cox[3] that such materials confer protection by competitive reaction with ozone, the antiozonant consumed at the surface of the rubber being replenished by diffusion from the bulk. This process has been termed "scavenging."

It has been inferred previously, from studies of the nature of the protection conferred by N,N'-dioctyl-p-phenylenediamine (DOPPD) that scavenging is not the operative mechanism.[2]

In support of this conclusion, the diffusion rate of DOPPD to the surface of a natural rubber vulcanizate has now been calculated and compared with the rate of incidence of ozone under conditions where the antiozonant is observed to be highly effective.

EXPERIMENTAL DETERMINATION OF THE DIFFUSION COEFFICIENT OF DOPPD IN NATURAL RUBBER

A sheet of vulcanized natural rubber, about 6 cm. square and ca. 0.08 cm. thick was immersed in DOPPD. The uptake (M_t) of DOPPD was determined as a function of time, until equilibrium swelling (M_∞) was attained. Classical diffusion theory[4] shows that until equilibrium is approached:

$$M_t/M_\infty = 2(Dt/\pi l^2)^{1/2}$$

where D is the diffusion coefficient and $2l$ is the thickness of sheet. Figures 1 and 2 show that a plot of M_t against $t^{1/2}$ is substantially linear, from which the diffusion coefficient D can be calculated.

It should be realized that for a system such as a swelling rubber the diffusion coefficient increases as the polymer swells.[4] Hence D is not a constant, and the above experiment determines an average diffusion coefficient $\bar{D}$
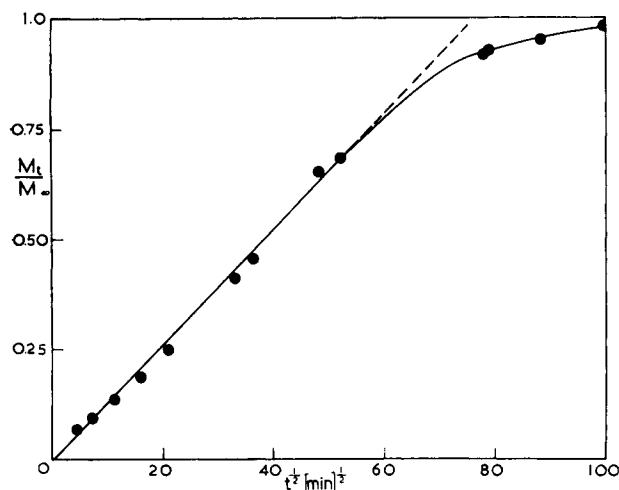
Fig. 1. Plot of DOPPD uptake M_t against $t^{1/2}$ at 20°C.
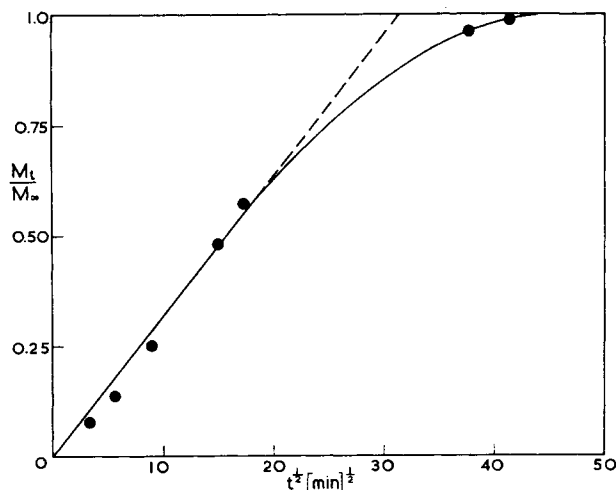
Fig. 2. Plot of DOPPD uptake M_t against $t^{1/2}$ at 50°C.

given by:

$$\bar{D} = (1/C_0) \int_0^{C_0} D(C)dC \qquad (2)$$

where C_0 is the equilibrium concentration per unit volume. Results obtained at 20°C. and 50°C. are given in Table I.

In the desorption process occurring when antiozonant migrates to the surface consequent on the surface reaction with ozone, the value of the average diffusion coefficient $\bar{D}'$ may be written as:

$$\bar{D}' = (1/C_0') \int_{C_0'}^{0} D(C)dC \qquad (3)$$

where C_0' is the concentration added to the rubber. From Table I it is seen that $C_0 \simeq 1.75$; now the concentration of DOPPD used to confer considerable protection at an ozone concentration of 0.2 mg./l. is 0.06. Since $C_0' << C_0$, then $\bar{D}' < \bar{D}$, since $D(C)$ increases with C.

TABLE I

Temperature, °C.	$\bar{D}$, cm.^{2} sec.$^{-1}$	C_0, g. cm.$^{-3}$
20	1.1×10^{-9}	1.7
50	7.5×10^{-9}	1.8

THEORY OF ANTIOZONANT MIGRATION

For the reaction of antiozonant with ozone at the surface of a plane sheet

$$dC/dt = -kaC \qquad (1)$$

where C is the concentration of antiozonant, a is the concentration of ozone, and k is the bimolecular rate constant of the reaction. It is assumed that the concentration of ozone at the surface of the rubber remains constant, as the self-diffusion coefficient of a gas greatly exceeds the diffusion coefficient of the antiozonant in the rubber.

Hence at the surface of the rubber:

$$C = C_0 e^{-\beta t} \qquad (2)$$

where

$$\beta = ka \qquad (3)$$

Thus it is required to solve:

$$\partial C/\partial t = D \, \partial_2 C/\partial x^2 \qquad (4)$$

with the following boundary conditions:

$$C = C_0 > x \to \infty, \, 0 \le t < \infty$$
$$C = C_0 e^{-\beta t} > x = 0, \, 0 \le t < \infty$$
$$C = C_0 > t = 0, \, 0 \le x < \infty$$

Solving by the Laplace transform,

$$C(x, t) = C_0 \left\{ erf \frac{x}{2\sqrt{Dt}} + e^{-\beta t}\left[e^{-ix\sqrt{\beta/D}} \right.\right.$$
$$erfc\left(\frac{x}{2\sqrt{Dt}} - i\sqrt{\beta t}\right) + e^{ix\sqrt{\beta/D}} \, erfc$$
$$\left.\left.\left(\frac{x}{2\sqrt{Dt}} + i\sqrt{\beta t}\right)\right]\right\} \quad (5)$$

where $i = \sqrt{-1}$

$$erf\,y = (2/\sqrt{\pi}) \int_0^y e^{-\eta^2} \, d\eta$$
$$erfc\,y = (2/\sqrt{\pi}) \int_y^\infty e^{-\eta^2} \, d\eta$$

Complex error functions[5] may be expressed in terms of the special functions $U(X, Y)$, $V(X, Y)$, defined by:

$$U(X,Y) + iV(X,Y) = e^{-z^2}\left[1 + (2i/\sqrt{\pi}) \int_0^z e^{t^2} \, dt\right]$$

where $z = X + iY$

Such functions have been tabulated by Carslaw and Jaeger[5] and by Rabinovitch.[6]

Equation (5) then becomes:[6]

$$C = C_0 \left[erf \frac{x}{2\sqrt{Dt}} + exp\left(\frac{-x^2}{4Dt}\right)\left(U \sqrt{\beta t}, \frac{x}{2\sqrt{Dt}}\right)\right] \quad (6)$$

To obtain the amount of antiozonant arriving at the surface per square centimeter per second (F_1), $F_1 = D(\partial C/\partial x)_{x=0}$ is applied to eq. (5), yielding finally:

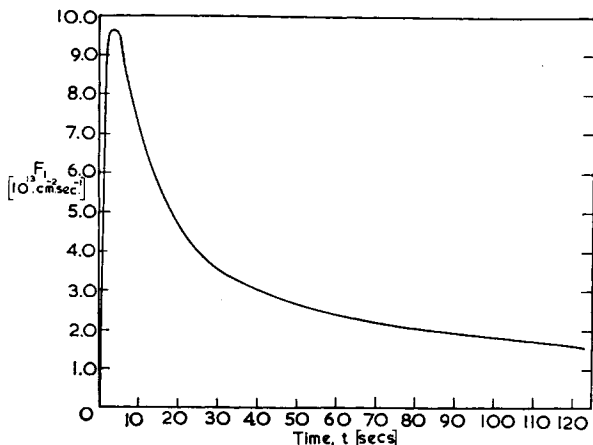$$F_1 = C_0 \sqrt{\beta D} . V(\sqrt{\beta t}, 0) \qquad (7)$$

Fig. 3. Plot of the function $F_1[= C_t\sqrt{\beta D}\,V(\sqrt{\beta}t,0)]$ against time.

Also, it can be shown that F_1 has a maximum value at $t = \tau$, where τ is given by

$$V(\sqrt{\beta\tau},\,0) = 1/\sqrt{\pi\beta\tau} \qquad (8)$$

The form of F_1 is shown in Figure 3.

CALCULATIONS

It has been shown experimentally[2] that 6% DOPPD confers substantial protection on a natural rubber vulcanizate at an ozone concentration of 0.2 mg./l. The rate of incidence of ozone molecules (F_2) is given by:

$$F_2 = a\sqrt{RT/2\pi M} \qquad (9)$$

where M is the molecular weight of ozone, T is the absolute temperature, and R is the ideal gas constant. In terms of the number of incident molecules, $F_2 \simeq 10^{20}$ cm.$^{-2}$ sec.$^{-1}$.

To calculate F_1, a value of $\beta = 0.25$ has been used. Hence, $(F_1)_{max} \simeq 10^{14}$ cm.$^{-2}$ sec^{-1} on the basis of eqs. (7) and (8). The value of β was estimated from the bimolecular rate for an olefin representative of natural rubber, 2-methylbut-2-ene,[7] which is 1.2×10^4 l. mole^{-1} sec.$^{-1}$; since the rate constant for DOPPD is about five times this value,[8] the value of k in eq. (3) is 6×10^4 l. mole^{-1} sec.$^{-1}$, from which β was calculated.

DISCUSSION AND CONCLUSIONS

It is clear that under conditions where the antiozonant is very effective, the calculated maximum diffusion rate at the surface is less than the rate of incidence of ozone by a factor of 10^6. Indeed, for reasons discussed above, this factor may be even larger due to the diffusion coefficient being overestimated by the experimental technique used.

Further, the theoretical treatment shows that the diffusion rate of antiozonant decreases quite rapidly with time after the maximum rate has been reached. Experiments on antiozonant action have not exhibited any time dependence.[2] Also, it was shown above (Table I) that at 50°C. the diffusion constant was about seven times that at 20°C.; detailed measurements of the behavior of DOPPD at 50°C. yielded results not significantly different from those obtained at 20°C.

The possibility therefore that a diffusion-maintained "scavenging" process is the relevant antiozonant mechanism of DOPPD seems precluded by the above considerations.

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