# Oxygen Barriers That Use Free Radical Chemistry

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*Oxygen barriers made of linoleic acid, ethyl cellulose and a cobalt catalyst can reduce oxygen penetration over 2,000 times compared with an ethyl cellulose barrier of the same thickness. The barrier is effective only when the product of linoleic acid concentration and barrier thickness exceeds a critical value, which is apparently necessary to effectively initiate the reaction. When this condition is met, the time that the barrier is effective can be predicted using a theory that assumes oxygen consumption is diffusion-controlled. Operating in this condition, the barrier is about 70% efficient, that is, about two-thirds for the double bonds available in linoleic acid react with oxygen. The results provide a rationale for the design of better oxygen barriers.*

## Introduction

Thin barrier films are often used as coatings or packaging to protect product properties. For example, paints retard corrosion, and food packaging guards food freshness. Films which retard oxygen or water have special value. For example, the coating on the dielectric layers used in many electronic devices tries to exclude water to insure product performance.

There are three chief routes to make better barrier films. The most obvious is to make a less permeable polymer. Polyvinylidene chloride is a good example. Because less permeable polymers have been subject to so much informed research, this route has been carefully and deeply developed (Brandrup et al., 1999). It is not the focus of this article.

The second route to a better barrier film is the incorporation of impermeable flakes into the film itself (Wakeman and Mason, 1979; Cussler et al., 1988). One such structure is the human skin, which has flakes of less permeable protein in a matrix plasticized with lipids (Michaels et al., 1975). In synthetic polymers, flakes of mica, clay, and nylon have all been used (Cussler et al., 1988; Michaels et al., 1975; Falla et al., 1996). Typically, the barrier properties can be improved about an order of magnitude using such flakes. However, we will not stress these flake-filled systems here.

The third route to a better barrier is the addition of chemically reactive groups within the film. Such reactive barriers are an active area of product development, leading to frequent patents (Speer et al., 1996; Katsumoto and Ching, 1998; Gauthier and Speer, 1999). These patents are a parallel development to extensive fundamental work, discussed in more detail below. Interestingly, these reactive groups do *not* affect the steady-state permeability of the barrier, but they can increase the time before significant permeability occurs. This increase can often be a factor of 100 or more, so this effect has considerable practical potential.

The increased time before permeability occurs obviously depends on the kinetics of any reactions. If the kinetics are too slow, there won't be much effect. If the kinetics are fast, then the increases in time before significant permeation can be predicted *a priori* from experiments without reactive groups (Yang et al., 2001). In these cases, a fast reaction is one in which time for diffusion is much greater than the time for reaction, that is, in which the second Damköhler number is much larger than one.

However, the many recent patents suggesting barrier films for oxygen depend on catalytic or photoinitiated reactions. The complex chemistry of these reactions means that the characteristic time of the reaction is a function of concentrations of reaction intermediates, which are themselves a function of how long the barrier has been in use. In this case, the prediction of the performance of these barrier films is more complicated.

In this article, we study one such oxygen barrier film. Oxygen diffusing across the film at first goes through almost unmolested. Some oxygen does react with double bonds in the film to produce hydroperoxides which in turn generate free radicals which consume more oxygen. Thus, the reaction is somewhat like a fire: while it is being lit, it consumes little oxygen; but once ignited, it reacts with all the oxygen which is available. It is the study of such a system which is the subject of this article.

Our study of these oxygen barriers differs in one profound respect from barriers normally described in the patent literature. These patents seeks chemistries which produce very effective barriers. In contrast, we seek chemistries which per-

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mit easy experiments in a reasonable amount of time. We do not want the oxygen barrier to be effective for months, but only for a few hours. Such shorter experiments will allow us to study expeditiously the mechanisms by which these barriers function.

To achieve this objective, we choose to study linoleic acid as a reagent catalyzed by cobalt and dissolved in a film of ethyl cellulose. The linoleic acid and the cobalt are features of one strong patent (Speer et al., 1996). However, the ethyl cellulose may seem a strange choice, for it is very permeable to oxygen and other gases. For example, it is ten times more permeable than polyolefins. We chose ethyl cellulose for exactly this reason: its high permeability makes quick experiments easier. Before reporting these experiments, however, we first review some relevant theory.

## Theory

To place our analysis on a more definite basis, we consider two gas volumes separated by a barrier film. One upstream volume contains a solute like oxygen, initially at a concentration of $C_{10}$. The other, downstream volume, which initially

**Table 1. Selection of Earlier Predictions of Lag Times***

| Case | Boundary Condition | Lag Time | Fast Reaction Limit | Remarks and Refs. |
|---|---|---|---|---|
| No Reaction | | | | |
| | Equilibrium | $\frac{\ell^2}{6D}$ | — | The basic case in all analyses, (Daynes, 1920; Frisch, 1957; Crank, 1975; Cussler, 1997; Paul and Yampolski, 1994). |
| | Resistance of $(1/k_D)$ | $\frac{\ell^2}{6D}\left[1+\frac{2}{1+\frac{\ell k_D}{P}}\right]$ | — | Not relevant here because there is no surface resistance (Gough and Leypoldt, 1980; Ash, 2001). |
| First-Order Reaction | | | | |
| Irreversible | Equilibrium | $\frac{\ell^2}{6D}\left[\frac{3(\phi\coth\phi-1)}{\phi^2}\right]$ | $\frac{\ell^2}{2\sqrt{kD}}$ | When the reaction becomes fast, the lag goes to zero (Astarita et al., 1983; Siegel, 1991); $\phi$ is the Thiele modulus. |
| Reversible | Equilibrium | $\begin{pmatrix}\text{Not known}\\ \text{analytically}\end{pmatrix}$ | $\frac{\ell^2(1+K)}{6D}$ | For an irreversible reaction, K and hence the lag are infinite (Frisch, 1957; Finger et al., 1960; Paul, 1969; Paul and Kemp, 1973; Paul and Koros, 1976; Vant-Hull and Noble, 1991). |
| Irreversible and Reversible | Equilibrium | $\frac{\ell^2(1+K)}{6D}\left[\frac{3(\phi\coth\phi-1)}{\phi^2}\right]$ | $\frac{\ell^2(1+K)}{6D}$ | A combination of the two previous cases with a more general Thiele modulus $\phi$ (Siegel, 1991). |
| Dissolution | | | | |
| | Equilibrium | 0 | — | Dissolving particles give no lag (Higuchi, 1961; Paul and McSpadden, 1976). |
| | Resistance of $(1/k_D)$ | $\left[\frac{C_{20}}{k_D C_2(\text{sat})}\right]^2 \frac{D}{2\frac{C_{20}}{C_2(\text{sat})}}$ | — | Not relevant here because there is no surface resistance (Higuchi, 1961; Paul and McSpadden, 1976). |
| Zero-Order Reaction | | | | |
| | Equilibrium | $\begin{pmatrix}\text{Not known}\\ \text{analytically}\end{pmatrix}$ | $\frac{\ell^2}{6D}$ | When the adsorbent is saturated, no change in lag is predicted (Paul, 1969; Paul and Kemp, 1973). |
| Second-Order Reaction | | | | |
| Irreversible | Equilibrium | $\begin{pmatrix}\text{Not known}\\ \text{analytically}\end{pmatrix}$ | $\frac{\ell^2}{2P}\left(\frac{C_{20}}{C_{10}}\right)$ | This is closest to the case investigated here (Yang et al., 2001). |

*Most assume first-order reversible reactions and so do not apply to the reactions emphasized in this article.

contains no solute, has a small solute concentration $C_{1\ell}$ at time $t$. This solute gain occurs because solute is transferred from the upstream volume to the film, permeates across the film, and then is transferred into the downstream volume.

We are interested in how $C_{1\ell}$ is affected by any chemical reactions. We can imagine three such limits. First, if there is no reaction, the concentration $C_{1\ell}$ will vary with time $t$ at large times as follows (Daynes, 1920; Frisch, 1957; Crank, 1975)

$$\frac{C_{1\ell}}{C_{10}} = \frac{AP}{V\ell}\left(t - \frac{\ell^2}{6D}\right) \tag{1}$$

where $A$ and $\ell$ are the barrier area and thickness, respectively; $V$ is the volume of the downstream compartment; and $P$ and $D$ are the solute's permeability and diffusion coefficient in the barrier. The quotient of these two is the partition coefficient $H$, the solubility of the solute in the film (Cussler, 1997). Note that the quantity ($\ell^2/6D$), called the lag time, depends on the diffusion coefficient $D$, not on the permeability $P$. Finally, at times equal or less than the lag time, the concentration is given by a more complex relation (Daynes, 1920).

The second interesting limit occurs when the reaction of the solute within the barrier is irreversible. Such a reaction is not first-order, because it involves a diffusing species and a second reacting species initially present only within the barrier. We assume that this reaction is instantaneous, that is, it is so fast that the two reagents cannot coexist (Crank, 1975; Astarita et al., 1983). In this case, the lag time is predicted to be (Yang et al., 2001)

$$\frac{C_{1\ell}}{C_{10}} = \frac{AP}{V\ell}\left(t - \frac{\ell^2 \upsilon c_{20}}{2PC_{10}}\right) \tag{2}$$

where $c_{20}$ is the initial concentration of immobile reagent in the membrane and $\upsilon$ is a stoichiometric coefficient, equal to the number of moles of solute consumed per mole of immobile reagent. Note that the quantity ($\ell^2 \upsilon c_{20}/2PC_{10}$) a different lag time, now depends on $P$, not on $D$. Note also that after the lag, $C_{1\ell}$ varies with $t$ at the same rate in Eq. 2 as in Eq. 1. These predictions have been verified without any adjustable parameters for fast acid-base reactions.

Parenthetically, the idea of using a chemical reaction to increase the lag time is about 50 years old, and has produced a rich and varied literature. Some of the important cases discussed in this literature are summarized in Table 1. One strong example of earlier investigation assumes that the solute is rapidly adsorbed by sites within the membrane. When this adsorption follows a Langmuir isotherm, the concentration varies as follows (Finger et al., 1960; Paul, 1969; Paul and Kemp, 1973; Paul and Koros, 1976; Vant-Hull and Noble, 1991)

$$\frac{C_{1\ell}}{C_{10}} = \frac{AP}{V\ell}\left(t - \frac{\ell^2}{6D}\left[1 + Kf(c_1)\right]\right) \tag{3}$$

where $K$ is the equilibrium constant of the chemical reaction and $f(c_1)$ is a known function of constants in the Langmuir isotherm. When $c_1$ is such that the isotherm is linear, $f(c_1)$ equals unity. When $c_1$ is such that the Langmuir isotherm is saturated, $f(c_1)$ is zero. In patented cases of barrier films, the reaction is irreversible so $K$ is infinity, suggesting that the lag time should be infinity. The reason for this incorrect prediction is that the Langmuir isotherm is a poor representation of fast, irreversible second-order reaction.

The cases in Table 1 also include situations where the lag results from other causes, including an additional surface resistance to mass transfer (Paul and McSpadden, 1976; Ash, 2001). Such a resistance might come from a coating on a pill that itself was a solid suspension of small drug particles. While such surface resistances are interesting, they are not involved in the experiments reported here. Here, we are interested in three cases: the classical case of no reaction, the case of a second-order instantaneous reaction, and a third case described next.

The third limit of interest here occurs when there is a chemical reaction with an immobile reagent, but that reaction autoaccelerates. In this case, what happens depends on the details of the chemical reaction. At first, reaction rate will be negligible, and the membrane will leak oxygen. After a while, the members will start to consume oxygen. If this consumption is modest, the membrane will still leak, but at a reduced rate. Alternatively, if the consumption truly autoaccelerates, then the membrane will consume any available oxygen. In this case, it may even consume oxygen which has already leaked across, causing $C_{1\ell}$ to go through a maximum. When the immobile reagent is finally exhausted, the membrane will go back to leaking oxygen at the original, nonreacting rate.

The reactions involved actually include the expected steps of initation, propagation and termination. More specifically, these are (Basolo and Pearson, 1967).

Initiation:

$$O_2 + RH \rightarrow ROOH$$
$$Co^{2+} + ROOH \rightarrow Co^{3+} + OH^- + RO\cdot$$
$$Co^{3+} + ROOH \rightarrow Co^{2+} + H^+ + ROO\cdot$$

Propagation:

$$RO\cdot + RH \rightarrow ROH + R\cdot$$
$$R\cdot + O_2 \rightarrow ROO\cdot$$
$$ROO\cdot + RH \rightarrow ROOH + R\cdot$$

Termination:

$$2ROO\cdot \rightarrow \text{Inactive products}$$

In these relations, RH is the hydrocarbon which contains the double bond.

We can approximate this chemistry as follows. At first, without reaction, the average oxygen concentration $c_1$ in the membrane is about $HC_{10}/2$. Because we expect any lag without reaction will be small, we neglect it. The downstream concentration then increases until $t_o$, when it is

$$C_{1\ell} = \left(\frac{PA}{\ell V}\right) C_{10} t_o \ll C_{10} \tag{4}$$

If the reaction now starts at a fast rate per volume of ($k\, c_{20}\, c_1$), almost all oxygen entering the membrane is consumed by this reaction

$$\left(\frac{P}{\ell/2}\right) AC_{10} = kc_{20}c_1(A\,\ell) \tag{5}$$

or

$$c_1 = \frac{2PC_{10}}{kc_{20}\,\ell^2} \tag{6}$$

Note that this implies that the average location of the reaction is about half way through the membrane. Whether oxygen concentration $C_{1\ell}$ goes through a maximum now depends on the ratio:

$$\frac{HC_{10}}{c_1} = \left(\frac{A\,\ell}{V}\right)\left[\frac{Hkc_{20}t_o}{2}\right] \tag{7}$$

where $H$ is the partition coefficient. If this ratio is less than one, the membrane will continue to leak. If it is greater than one, the downstream concentration $C_{1\ell}$ will go through a maximum.

Thus, whether or not there is a maximum depends both on reaction parameters (in brackets) and on experimental geometry (in parentheses). In particular, Eq. 7 suggests that a line where ( $\ell c_{20}$) is a constant should divide the results into two classes: those with a slow leak, and those where the downstream concentration goes through a maximum. We will test this suggestion in the experiments below.

## Experimental Studies

Ethyl cellulose (Aldrich), toluene (Aldrich), linoleic acid (Aldrich), and cobalt Hex-Cem (the cobalt salt of 2-ethylhexanoic acid in a mineral spirits carrier, Sigma) were all reagent grade and were used as received, without further purification. Oxygen and nitrogen (Air Products) had purities of 99.99% and 99.9%, respectively. Ethyl cellulose membranes were made in a dry box containing less than 50 ppm oxygen by preparing a 6% ethyl cellulose solution in toluene. After 1 $\mu$m ultrafiltration, the solution was cast on a Teflon plate. The resulting film was dried in the box overnight. Membranes containing linoleic acid and cobalt, prepared with the same method, were complely clear. Membranes containing the cobalt salt were purple; if the membranes were left in air, the color disappeared due to the chemical reactions involved. The membrane thickness was measured using a micrometer to an accuracy of $\pm 1$ $\mu$m.

Gas permeation through these membranes was measured in the diaphragm cell (Cussler, 1997; Yang et al., 2001) shown in Figure 1. The brass cell consists of two compartments, each of which has a volume of 24.7 cm$^3$. A brass plate with 24 evenly distributed holes 1 mm in diameter was used to support the low-pressure side of membrane. A brass ring supported the other high-pressure side. Rubber gaskets between the supports and the cell guaranteed that no leak occurred in the radial direction. The two compartments were held together with long bolts and sealed with "O" rings. Pressure transducers (Cole-Parmer Model 07356-61), which transfer the pressure into voltage, measured the pressure in each compartment. The transducers were accurate to $\pm 0.01$ psi, as calibrated with a digital pressure gauge (Cole-Parmer Model 68950-00).

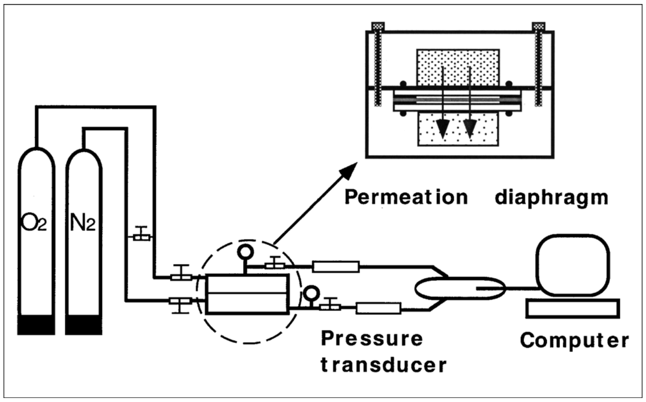

**Figure 1. Cell apparatus.**

The brass cell initially contains equal pressures of nitrogen in its two compartments. At time zero, oxygen is added to the upper compartment, and both compartment pressures are measured vs. time.

To make an experiment, we cut the membrane in the drybox to the desired size. After measuring its thickness, we installed it in the permeation cell. We fastened the bolts to seal the two compartments. While this took about 6 min., no obvious color change occurred in the membrane due to its exposure to air in this period. After the installation is finished, both upstream and downstream compartments were flushed with nitrogen for 10 min. We kept the upstream pressure higher than the downstream pressure during and after flushing, allowing nitrogen to permeate through the membrane for an additional hour to eliminate any oxygen. We flushed again, and then filled both compartments with nitrogen at one atmosphere. Next, we slowly introduced oxygen to the upstream compartment and started the data acquisition system to record the pressure in each compartment as a function of time. Experiments with pure ethyl cellulose films typically lasted about an hour. Experiments with reactive membranes, on the other hand, often lasted several days.

## Results

The experiments made as part of this work can be most easily reported in two groups. The first group illustrates the general characteristics of the barriers themselves. The second group tests the analysis sketched in the theoretical section above.

The first group of illustrative experiments includes studies of nonreactive membranes like those shown in Figure 2. The figure gives the concentration $C_{1\ell}$ in the downstream compartment as a function of time. This concentration is always less than 6% of that in the upstream compartment. The data in the inset show that experiments on different membranes of the same thickness are reproducible to within $\pm 5\%$. Results for different gases in the body of the figure show that these membranes are about twice as permeable to oxygen as to nitrogen. This selectivity suggests that the membranes are pinhole free, functioning by the diffusion-solubility mechanism (Cussler, 1997). The permeability of oxygen in ethyl cellulose from the slope of the data in Figure 2 is $1.8 \times 10^{-7}$

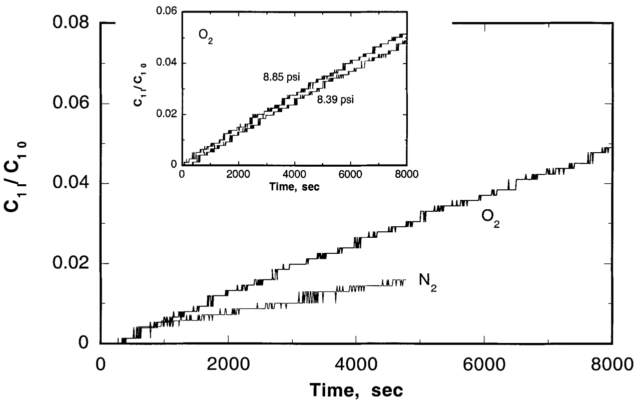

**Figure 2. Permeation across ethyl cellulose films.**

The permeability inferred from these data is 50% higher than that in the literature (Brandrus et al., 1999).

cm$^2$/s, higher than the value of $1.2\times10^{-7}$ cm$^2$/s given by Brandrup et al. (1999). We suspect this difference reflects residual solvent in our membrane. Because our interest is in the change in permeability caused by chemical reaction, this discrepancy is not a major issue. Experiments like those in Figure 2 suggest that the lag time ( $\ell^2/6D$) given in Eq. 1 is less than 30 s. We estimate the lag time from literature data (Brandrup et al., 1999) to be about 12 s, consistent with our observations.

The change caused by a reaction within the barrier film is illustrated by the results in Figure 3. This figure plots the concentrations of both upstream and downstream compartments as a function of $t/\ell^2$. This abscissa is used so that the 68 $\mu$m nonreactive membrane and the 84 $\mu$m reactive membrane can be more sensibly plotted on the same graph. The nonreactive membrane, plotted as the circles, shows the expected behavior: as the concentration in the upstream compartment drops, the concentration in the downstream compartment rises. Because the upstream and downstream volumes are the same, the sum of these concentrations is a constant.

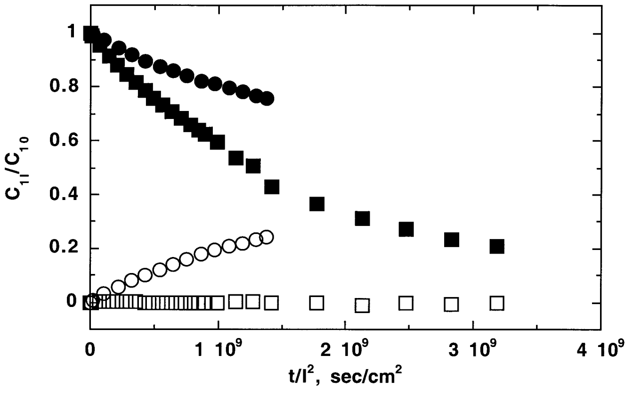

**Figure 3. Nonreactive vs. reactive films.**

The concentrations are plotted vs. time for both the upper and lower compartments (filled and open symbols, respectively). For the nonreactive films (circles), the concentrations in the upper and lower compartments change symmetrically. For the reactive film (squares), the concentration in the upper compartment drops quickly, but that in the lower comparment stays near zero.

The behavior of the reactive membrane is very different, as shown by the squares in Figure 3. The concentration in the upstream compartment drops faster than in the nonreactive case, a consequence of the reaction consuming oxygen inside the barrier. The concentration in the low-pressure compartment stays near its initial value of zero. At first glance, this looks like some sort of experimental error, a failure to close the mass balance on oxygen. In fact, oxygen *is* disappearing because of the chemical reaction.

Experiments like those in Figure 3 show that these barrier films are working. However, in many commercial applications, we want to know how low the oxygen concentration stays on the low-pressure side of the film. We want to know how close it is to zero. To explore this, we turn to the second group of experiments, those which also test the analysis given above.

We begin by considering the ratio suggested by Eq. 7. This ratio is based on the assumption that the oxygen consuming reaction does not begin at time zero, but only after some time $t_o$. The resulting analysis suggests two types of behavior. When the product of the thickness $\ell$ and the reagent concentration $c_{20}$ is less than a critical value, the membrane leaks oxygen, although more slowly than without reaction. When this product is greater than this critical value, the barrier first leaks oxygen, then recaptures this leaked oxygen, and finally fails dramatically. Thus, the downstream oxygen concentration is predicted to show a maximum when $\ell c_{20}$ exceeds a critical value.

We do observe both types of behavior, as shown in Figures 4 and 5. In Figure 4, the concentration rises with time for both the nonreactive and the reactive barrier. It rises about five times more slowly for the reactive film than in the nonreactive film, but it does rise. In Figure 5, the concentration first rises, but then drops. After 16 h, the concentration rises abruptly. This is a dramatic, but reproducible, change from an expected lag of less than 30 s for this thickness of membrane.

That these two behaviors are separated by a critical value of $\ell c_{20}$ is shown in Figure 6, which plots eighteen experi-

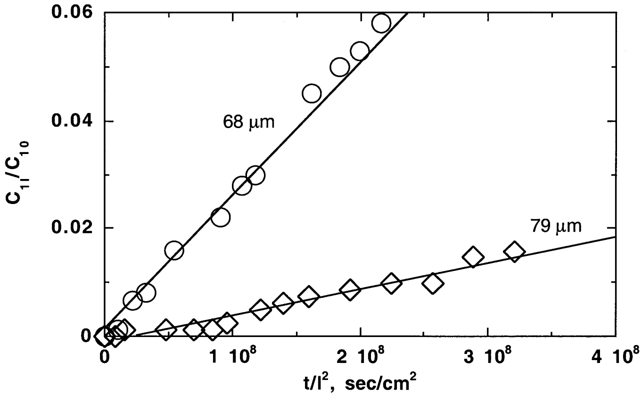

**Figure 4. Reactive film with a reduced leak.**

The flux across the 79 $\mu$m reactive film, shown as diamonds, is five times slower than in the 68 $\mu$m nonreactive film, shown as circles. In this case, the reaction consuming oxygen remains slow.

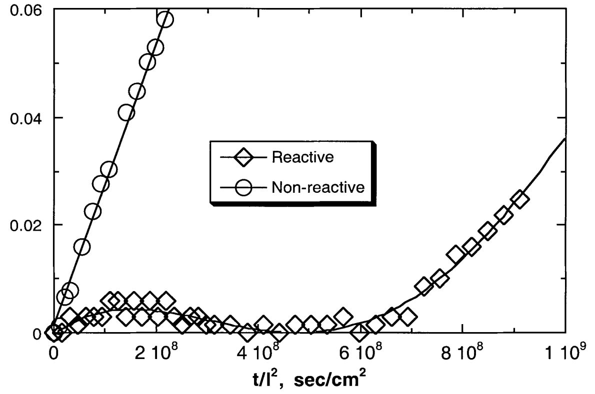

**Figure 5. Reactive film with a lag.**

The reactive film, shown as diamonds, excludes oxygen more effectively than the nonreactive film, shown as circles. Unlike the data in Figure 4, this 107 μm reactive film shows a lag of about a day, far longer than the 30 s of the 68 μm nonreactive film.

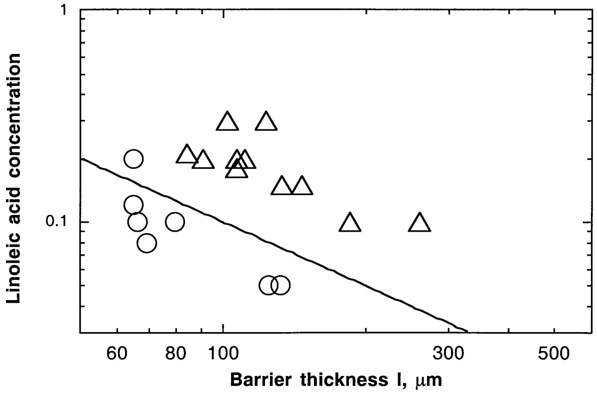

**Figure 6. Difference between leaks and lags.**

Behavior like that in Figure 4, shown as circles, occurs when the product of thickness and the linoleic acid concentration (as wt. %) is less than a critical value. Behavior like that in Figure 5, shown as triangles, occurs when this product is greater than this critical value.

ments using different values of $\ell$ and $c_{20}$, where $c_{20}$ is given as the mass fraction of linoleic acid. Experiments showing a leak like that in Figure 4 are shown as circles; experiments showing a maximum like that in Figure 5 are shown as triangles. Only one experiment is not separated by the criterion that $\ell c_{20} = 13.0$ μm; we believe that this barrier was flawed, and so leaked.

## Discussion

The results show how a membrane of ethyl cellulose and linoleic acid can function as an oxygen barrier. We organize our discussion of this barrier around four questions:

(1) Can this film be a good barrier?
(2) Can its barrier properties be predicted?
(3) How efficient is the barrier?
(4) When will the barrier function less effectively?

Answers to these questions are discussed in the following paragaphs.

*Can this film be a good barrier?* The answer to this question is yes, but subject to qualifications. As an example, imagine we have a 100 μm film of ethyl cellulose. Oxygen will begin leaking through this film after a lag time given by Eq. 1 as

$$\frac{\ell^2}{6D} = \frac{(0.01 \text{ cm})^2}{6(0.64\times 10^{-6} \text{ cm}^2/\text{s})} \doteq 30 \text{ s} \tag{8}$$

If, on the other hand, the film contains 0.2 g/cm³ linoleic acid, then the lag time is about $6\cdot 10^4$ s, as shown in Figure 5. Thus, the barrier properties of the film have been improved by 2,000 times.

We should stress that similar improvements should be possible for other less permeable films. We choose to study ethyl cellulose because it is a poor barrier, and hence gives quick, convenient experiments. If we choose a polymer which is a good barrier and hence less permeable, we expect correspondingly large improvements in the time before oxygen penetrates through the membrane. While these improvements may not always be as large as in this case, we expect that they will routinely exceed two orders of magnitude.

This attractive behavior does require activating the membrane so that it will consume oxygen. In this case, this implies that the product of reagent concentration and thickness exceed a critical value, as suggested in Figure 6. Moreover, even when this value is exceeded, the membrane may leak a little before it consumes the oxygen that has leaked (cf. Figure 5). Thus, the barrier film must become active quickly to be truly effective.

*Can these barrier properties be predicted?* The answer to this question is yes, but again with qualifications. The existing theory has two main predictions, that the lag is dramatically increased, and that the permeability after the lag is not dramatically altered. We will consider this second prediction first.

The second prediction that the permeability after the reaction is unaltered is not supported by the data in Figure 5. The permeability of this film, containing 0.2 g/cm³ linoleic acid, is reduced about four times by exposure to oxygen. In particular, the slope after the lag in Figure 5 corresponds to a permeability of $0.5\times 10^{-7}$ cm²/s; in contrast, the slope for the nonreactive data in Figure 2 corresponds to a permeability of $1.8\times 10^{-7}$ cm²/s. This smaller permeability is also reflected in the much more brittle character of the exposed film. What probabily is happening is that some of the linoleic acid is polymerizing because of hydroperoxide radicals caused by exposure to oxygen. This polymerization generates a more glassy, less permeable barrier in the exhausted region within the film.

The first prediction of the existing theory, that the lag is given by Eq. 2, assumes that oxygen must diffuse across this exhausted region to react. This exhausted region has the lower permeability caused by reaction. The lag in this film can be estimated from Eq. 2

$$\frac{\ell^2 \upsilon c_{20}}{Pc_{10}} = \frac{(0.01 \text{ cm})^2\, 2\left(\dfrac{0.2 \text{ g}}{\text{cm}^3}\cdot\dfrac{\text{mol}}{280 \text{ g}}\right)}{\left(0.5\times 10^{-7}\dfrac{\text{cm}^2}{\text{s}}\right)\left[\dfrac{8}{14.7}\,\dfrac{\text{mol}}{22.4\times 10^3 \text{ cm}^3}\,\dfrac{273}{298}\right]}$$
$$= 7\times 10^4 \text{ s} \tag{9}$$

This is in excellent agreement with the value of $6.5\times10^4$ s found from four experiments on such a membrane. In this estimate, we have used the permeability of $0.5\times10^{-7}$ cm$^2$/s found from Figure 5, rather than the permeability of $1.8\times10^{-7}$ cm$^2$/s found for films which have not undergone chemical reaction. We have assumed the membrane is 100% efficient; however, this is not true, as we show below.

However, we still successfully predict that the increase in lag time caused by oxygen consumption is large. If we use the oxygen permeability from an unreacted membrane, we will predict a 500 fold increase. If we use the correct permeability of the reacted film, we will be close to the observed increase in lag of 2,000 times. We can make this prediction without knowing the detailed chemistry necessary to activate the membrane.

*How efficient is the barrier?* To see how efficient this barrier is, we compare the amount of oxygen consumed with the maximum amount of oxygen which could react with the linoleic acid available. The maximum amount of oxygen which could be consumed is simply proportional to the moles of double bonds present in the membrane. As an example, we consider the 107·m membrane containing 0.2 g/cm$^3$ of linoleic acid used to get the results in Figure 5

$$\begin{aligned}\begin{pmatrix}\text{moles double}\\ \text{bonds}\end{pmatrix} &= 2\,\ell A c_{20}\\ &= 2(0.0107\text{ cm})6.15\text{ cm}^2\left[\frac{0.20\text{ mol}}{\text{cm}^3\ 280\text{ g}}\right]\\ &= 10\times10^{-5}\text{ mol.}\end{aligned}\tag{10}$$

The amount of oxygen actually consumed is easily found from the pressure drop in the upstream compartment, which is 7 kPa for the experiment shown in Figure 5. As a result

$$\begin{aligned}\begin{bmatrix}\text{moles O}_2\\ \text{consumed}\end{bmatrix} = \frac{V\Delta p}{RT} = \left[\frac{24.7\times10^{-6}\text{ m}^3 7\times10^3\text{ Pa}}{\dfrac{8.31\text{ Pa}\cdot\text{m}^3}{\text{mol}\cdot\text{K}}298\text{ K}}\right]\\ = 7\times10^{-5}\text{ mol}\end{aligned}\tag{11}$$

Thus, the membrane is about 70% efficient: about seven of every ten double bonds react to consume oxygen. The other three double bonds are probably consumed by polymerization, causing an interpenetrating network of polymerized linoleic acid within the ethyl cellulose.

*When will the barrier be less effective?* In general, reactive barriers will be effective when the reaction kinetics are fast. In more quantitative terms, this means that the second Damköhler number *Dm* is large (Yang et al., 2001)

$$Dm = \frac{\ell^2 k}{D} \gg 1 \tag{12}$$

While oxygen reacts rapidly with linoleic acid once free radicals are present, such radicals are initially absent, so the reaction kinetics are not initially fast. In this case, we expect that the reaction rates may initially be unable to meet the condition in Eq. 12. We can't make an *a priori* prediction without more chemical detail than we normally have available.

To make estimates without chemical detail, we have assumed the kinetics are slow for some time $t_o$, and then become fast and first-order in both oxygen and reagent, in this case linoleic acid. This assumption leads to the prediction in Eq. 7 that the product of thickness and reagent concentration ($\ell\, c_{20}$) has a critical value. If this value is exceeded, the barrier will operate in the fast reaction limit. If this value is not exceeded, the barrier will slowly leak.

We found evidence of this critical ratio in the data shown in Figure 6. Thus, for systems like this one, we could seek such a critical value in preliminary experiments, and use it as a guide to design better barriers. Before doing so, however, we need to check our ideas with experiments on other barrier chemistries.

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## Notation

$A$ = area
$c_1, c_{20}$ = concentrations of oxygen and immobile reagent inside the barrier, respectively
$C_2(\text{sat})$ = saturation concentration of a dissolving solute
$C_{10}, C_{1\ell}$ = concentrations of oxygen in the upstream and downstream compartments, respectively
$D$ = diffusion coefficient
$Dm$ = Damköhler number, equal to $\phi^2$
$H$ = partition coefficient
$k$ = reaction rate constant
$k_D$ = mass transfer coefficient at membrane surface reaction
$K$ = equilibrium constant for chemical reaction
$\ell$ = barrier thickness
$P$ = permeability
$t$ = time
$t_o$ = time where reaction becomes significant
$V$ = volume of one compartment in the diaphragm cell
$\upsilon$ = stoichiometric coefficient
$\phi$ = Thiele modulus, usually $\ell\sqrt{k/D}$

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