

## Absorption of Oxygen by Supported Films of Polyethylene\*

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### INTRODUCTION

The chemical absorption of oxygen by polyethylene and other polymers has been studied by a number of authors using a variety of techniques. The oxygen absorption reaction, for example, was studied with rubber at relatively low temperatures.<sup>1</sup> This involved suspending the rubber film sample from a hook in the reaction chamber. This technique is not suitable for studying the oxidative behavior of polyethylene at temperatures near or above its melting point because the unsupported, molten polymer will tend to flow under the influence of gravity, and relatively thick pockets of resin will form at low points in the apparatus. It has been reported that gas diffusion inward from the surface of the resin will take place only to depths of a few mils without limiting the rate of reaction.<sup>2-5</sup> The presence of thicker sections such as would be caused by polymer flow, especially when irregular in their occurrence, would compromise the reliability of the rate measurements obtained. The technique developed at the Bell Telephone Laboratories has been to contain the molten polyethylene in an aluminum boat, with oxygen reacting first at the surface (constant area) of the polyethylene, and then inward to a depth determined by the diffusion rate.<sup>2</sup> In this technique, sample weight is not considered, and the volume of oxygen absorbed is meaningful only as related to the surface area. An improvement on this method was suggested by Wilson.<sup>3</sup> His technique consists of placing alternate layers of glass wool and powdered resin in a cartridge. When this cartridge is raised to the reaction temperature, the resin melts and is presumed to flow along the fibers of the glass wool, thus giving a thin film of maximum surface. This method has the advantage of being able to relate oxygen absorption to sample weight. However, the desired disposition of molten polymer on the glass wool

fibers may or may not be achieved. Beachell and Nemphos<sup>4</sup> dissolve the polymer in carbon tetrachloride and cast films of 0.005-0.008 in. thickness either on rock salt plates or on the surface of mercury. However, it is stated that, without any support for these films at elevated temperatures, the molten polyethylene has a tendency to pool, causing difficulty in the control of sample thickness.

### EXPERIMENTAL

The device used in our studies to obtain a sample suitable for use above the melting point of the resin is the deposition of thin films of the polymer upon supporting metal screens. The metal screens employed do not exceed twelve mils in thickness, thereby permitting the oxygen to penetrate the sample by diffusing inward six mils from the top and bottom surfaces. The metal screening serves to prevent flow of the molten resin, which adheres among the meshes. After each reaction is complete, sample thickness is checked in order to insure that no flow has occurred. A dual purpose is served by the metal screen: it supports the resin, and, more especially, its thickness serves to govern the thickness of the molten resin film. Metal screens have been used as supports in oxygen absorption studies on rubber.<sup>6</sup>

Our samples are prepared by pressing about 0.1 g. of the powdered resin into a metal screen having an area  $\frac{3}{4} \times 3$  in. with the use of a heated Carver laboratory press. Conditions of temperature, pressure, and time are so chosen as to permit the resin sample to flow and to compress the molten sample to the desired film thickness. Typical conditions for conventional polyethylenes are 125°C. and 10,000 psi for 10-30 sec.

The oxygen absorption apparatus used in the present study is shown in Figure 1. It permits the measurement of oxygen gas absorbed under conditions of constant temperature and constant pressure. It includes the use of an Abderhalden drying pistol as the reaction chamber, along with a gas-

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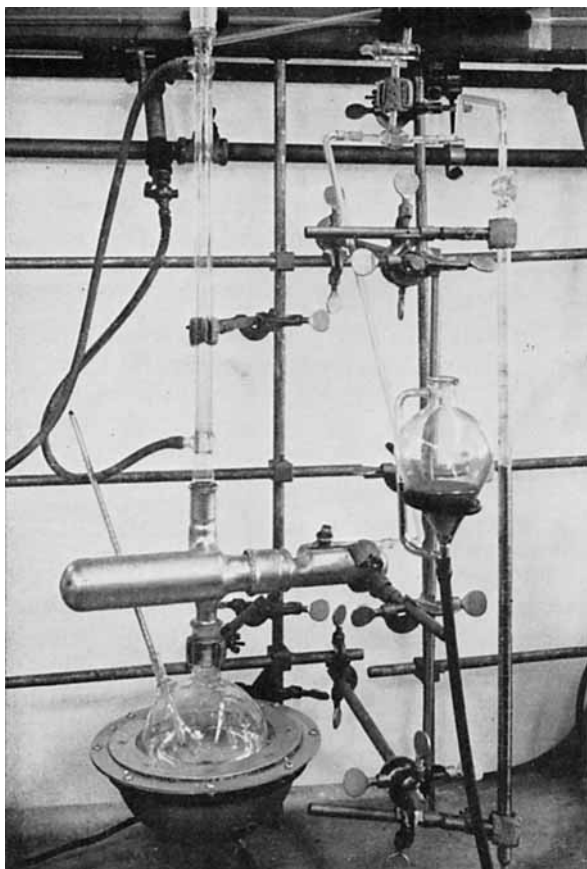


Figure 1.

measuring buret and mercury-leveling bulb. The choice of refluxing liquid governs the reaction temperature. Thus, the use of  $\alpha$ -methylstyrene gives a reaction temperature of  $166^\circ\text{C}$ ., cumene a temperature of  $152.5^\circ\text{C}$ ., and *p*-xylene,  $139^\circ\text{C}$ . The temperatures actually achieved within the reaction chamber were measured by using maximum-point recording Anschütz thermometers. A 10-g. charge of Zeolite-type adsorbent (Linde Molecular Sieve No. 5A) is placed into the pistol. The use of adsorbent agent is important, because unadsorbed gaseous reaction product will occupy volume in the reaction flask and will be measured as unreacted oxygen gas. The absorption of oxygen by polyethylene is catalyzed by light. The reaction chamber is, therefore, coated externally with aluminum paint in order to exclude light from the reaction environment. Figure 2 shows a detailed view of the apparatus with the metallic screen being placed into the reaction chamber. We did not find it necessary in our study to employ a water thermostat for the measuring burets as did Bolland,<sup>7</sup> nor to correct our oxygen absorption figures for variations in at-

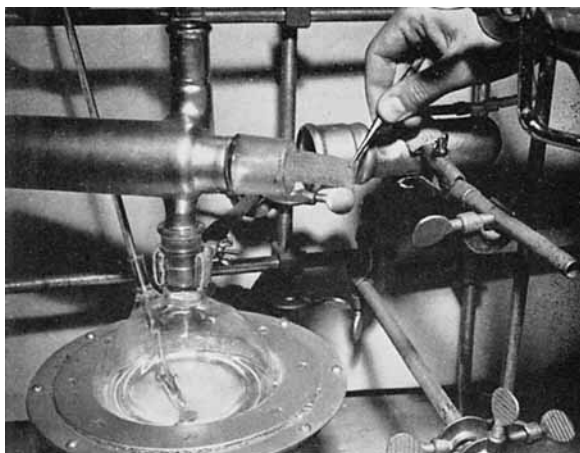


Figure 2.

mospheric pressure or in ambient temperature as did Wilson.<sup>3</sup>

#### EFFECT OF METALS

It is known that metals and metallic ions exert an influence on the oxidation of polyethylene.<sup>8</sup> Therefore, the nature of the metallic screen becomes of importance. Figure 3 shows the effect of different

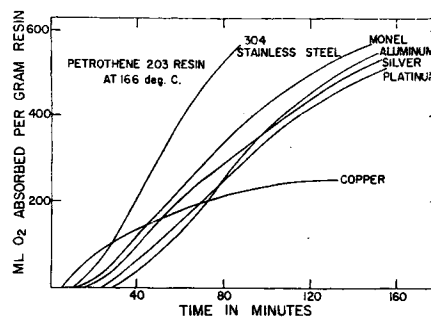


Fig. 3. Effect of different metal screens on oxygen absorption.

metallic supporting screens. Copper shows the same inhibitory effect which it exhibits in many free radical reactions. Stainless steel shows a pronounced catalytic effect, and platinum, generally considered to be inert to free-radical attack, occupies an intermediate position. Monel metal which we have chosen for our studies for reasons of availability and economy, very closely parallels platinum in its oxygen-absorption characteristics. The Monel screening used is  $40 \times 40$  mesh, calendered to 12 mils, and obtained from the Cleveland Wire Cloth and Manufacturing Co., Cleveland, Ohio. It was cleaned by washing in benzene, followed by air drying prior to use.

### STABILITY OF METHOD

Using this method, we find the same phenomenon of dependency of reaction rate upon temperature that is found for the more conventional methods which do not involve use of metallic screens. This is shown in Figure 4.

Studies of this type reflect in the length of the induction period obtained the degree of antioxidant protection present in the resin. Indeed, oxygen absorption measurements on polyethylene have been used chiefly in evaluating antioxidants. Figure 5

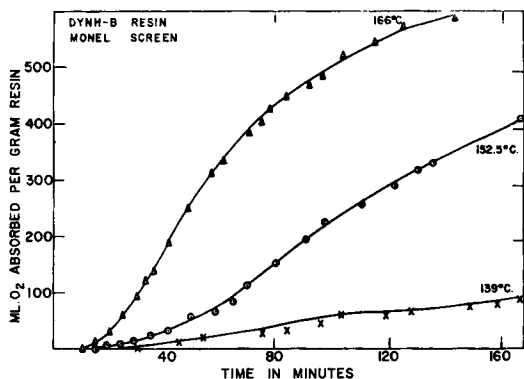


Fig. 4. Effect of temperature on oxygen absorption.

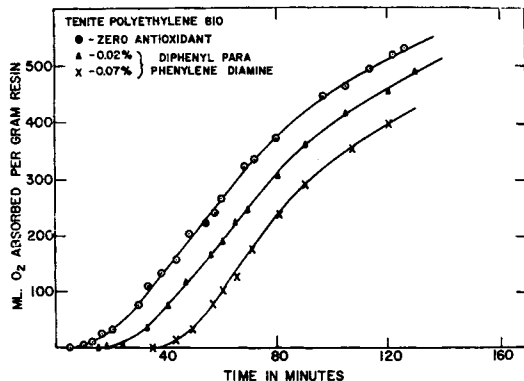


Fig. 5. Effect of antioxidant content on length of induction period.

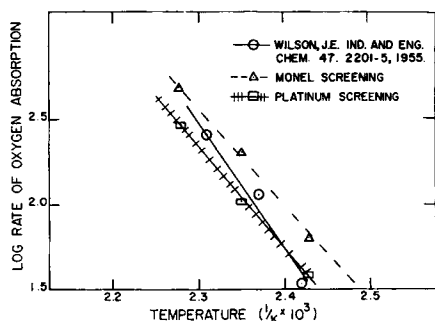


Fig. 6. Energy of activation of DYNH-B resin.

shows that the use of supporting metal screens is suitable for such a study. The induction period caused by 0.07% antioxidant is not  $3\frac{1}{2}$  times as long as that observed in the presence of 0.02% antioxidant. This lack of linearity between antioxidant concentration and the length of the induction period has been observed previously.<sup>9</sup>

Wilson, using his recommended procedure, obtains results for DYNH-1 Blend B polyethylene which indicate that the energy of activation for the reaction governing the steady state condition is 35 kcal./mole.<sup>3</sup> Results obtained on an identical sample of resin by our method yield an energy of activation of 30 kcal./mole. A comparison of our results with Wilson's are afforded by Figure 6.

### DIFFERENTIATION AMONG POLYETHYLENES

Subjecting a series of commercial polyethylenes to the action of oxygen gas at elevated temperatures by use of the procedure described in the present

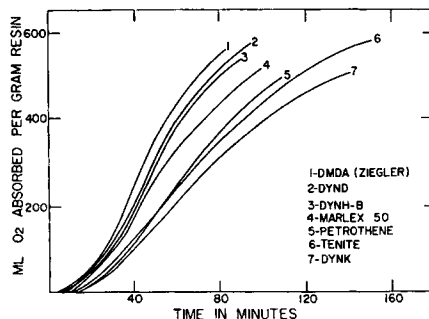


Fig. 7. Oxygen absorption by polyethylene resins at 166°C.

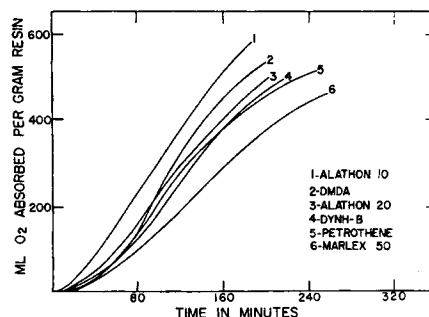


Fig. 8. Oxygen absorption by polyethylene resins at 152.5°C.

work results in a differentiation among these polymers, as shown in Figure 7. The relative position of these resins does not reflect the stability inherent in the resin itself, since the amount and type of antioxidant varies. The relative order of oxidizability depends upon temperature. Thus we see that Marlex 50 resin at 166°C. absorbs oxygen more

rapidly than does Petrothene 203-E-38 resin. Figure 8, however, shows that this relationship has been reversed at a lower temperature (152.5°C.).

## FACTORS AFFECTING OXIDIZABILITY

### Branching

Since the attack by oxygen upon polyethylene is free radical in nature, it is to be expected that tertiary hydrogen atoms, which are more readily attacked by free radicals than are secondary hydrogens, will prove more susceptible to oxidation. On this basis, polyethylene resins with more branching can be expected to absorb oxygen more readily.

differ from one another only in their degree of unsaturation. Suitable polymeric substrates are to be found in the Phillips Chemical Company's Hydropols, polybutadiene polymers that are hydrogenated to different degrees to give molecular species differing only in their extent of unsaturation.<sup>10</sup> Three such materials were measured for their oxygen absorption propensities. The results are presented in Figure 10. If, as is common in all kinetic studies, only the earlier portions of the curves are considered, then there is not obtained the expected correlation of extent of unsaturation with ease of oxidation. Such a correlation is, however, apparent if one relates unsaturation with the onset

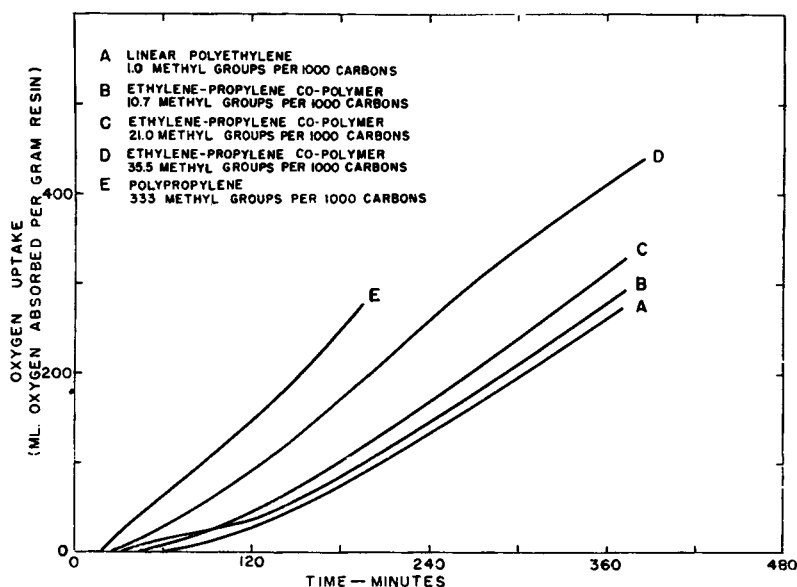


Fig. 9. Effect of methyl branching upon oxygen absorption at 139°C.

To test this principle, copolymers of ethylene and propylene, identical in degree of unsaturation and, presumably, in molecular weight but differing in the number of branches and, therefore, in the number of tertiary hydrogens, were examined for their absorption of oxygen. Along with these materials there were tested specimens of polypropylene and linear polyethylene. The results, shown in Figure 9, indicate that the expected relationship between branching and oxidizability is obtained.

### Unsaturation

Studies by Bolland and co-workers<sup>7</sup> at the British Rubber Producers Laboratories have shown that unsaturation in organic molecules is primarily responsible for rapid oxidizability. It occurred to us to test this by use of polyethylenelike models which

of diminution of oxygen absorption as shown by the last portions of these curves.

The apparent cessation of oxidation indicated by the abatement of oxygen consumption as shown in these curves is an unlikely occurrence. A creditable rationalization of this experimental phenomenon can be made by assuming that the leveling-off is caused by the accumulation of unadsorbed reaction products, such as carbon monoxide, carbon dioxide, and water, occasioned by the unusually rapid Hydropol oxidation. It is known that carbon monoxide is a product of polyethylene oxidation, and that it is only incompletely adsorbed by the Molecular Sieve adsorbent used.<sup>11</sup> The consequences of this conceivable explanation are important, for they signify that the order in which the absorption curves of Figure 10 level off reflects

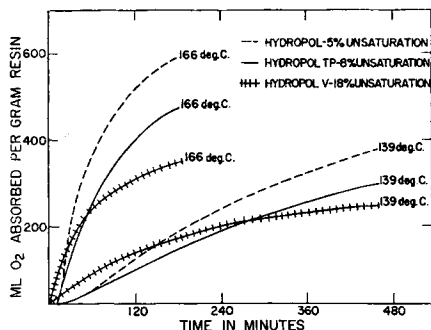


Fig. 10. Oxygen absorption by hydrogenated polybutadienes.

the relative rate at which oxidative products are produced. The determination of extent of polyethylene oxidation by measurement of oxidation product concentration is not unusual.<sup>12</sup> Thus, the apparent fall-off in oxygen consumption serves as an index of polymer oxidizability. On this basis, our experimental results confirm Bolland's conclusions relating unsaturation and oxidizability.

### Molecular Weight Distribution

Hydrocarbon oxidation reactions can be described as operating on the weak-link-in-the-chain principle. Given an organic molecule with different functional groups, oxidation will occur at those points in the molecule which are most susceptible to free radical attack by oxygen. This being the case, there has been no reason to believe that molecular size parameters influence the oxidative rates of hydrocarbons. An opportunity to test this premise is afforded by two DuPont polyethylene resins, namely Alathons 10 and 20. These have identical weight-average molecular weights, but differ in the degree of molecular weight spread; Alathon 10 having a broad distribution of molecular weight and Alathon 20 having a narrow distribution. As far as is apparent from their infrared absorption spectra, these resins have identical

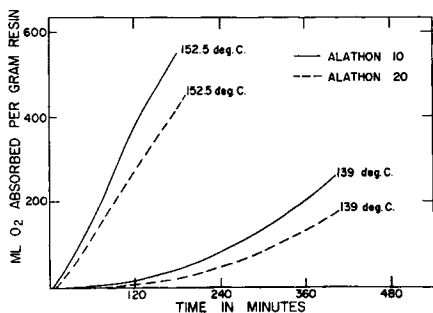


Fig. 11. Oxygen absorption by Alathon 10 and Alathon 20.

molecular structures. Nevertheless, these polymers are found to differ in their rates of oxygen absorption, as indicated by Figure 11.

It is concluded that some factor relating to molecular weight distribution affects polymeric hydrocarbon oxidizability. In all probability this relates to the influence of endgroups, the number of these present being governed by the molecular weight distribution.

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### Synopsis

It is shown that the elevated temperature study of oxygen gas absorption by polyethylene resins is freed of the troublesome flow of polymer by the use of thin supporting metallic screens whose thickness defines the depth of the molten resin

specimen. The influence of the screen composition on reaction rate is measured for several metals. The oxygen absorption reaction with the use of supporting Monel metal screens exhibits the classical response to free radical inhibitors and has the same energy of activation that characterizes the absorption reaction without screen. Using the device of supporting screens in a simplified oxygen gas absorption apparatus made from a modified Abderhalden drying pistol, we found that methyl branching predisposes to resin oxidizability in the expected manner. Unsaturation, however, does not correlate experimentally with oxygen absorption curve. In addition, a parameter related to molecular size, probably the polymeric endgroups, is seen to influence polyethylene oxidizability.

### Résumé

Il a été montré qu'à température élevée l'étude de l'absorption de l'oxygène par des résines de polyéthylène est débarassée de l'écoulement gênant du polymère par l'emploi de minces écrans métalliques comme supports. L'épaisseur de ces écrans détermine celle de l'échantillon de résine fondue. L'influence de la composition de l'écran sur la vitesse de réaction a été étudiée pour divers métaux. L'absorption d'oxygène à l'aide d'écrans supports en métal-monel répond à la théorie classique des inhibiteurs de radicaux libres et possède une énergie d'activation égale à celle qui caractérise la réaction d'absorption sans écran. Grâce à l'emploi d'écrans supports dans un appareil d'absorption de l'oxygène simplifié et construit au départ d'un pistolet sécheur d'Abderhalden modifié, il a été possible de mettre en évidence une prédisposition à l'oxydabilité des résines possédant des groupes méthyles latéraux. Ce résultat répond de façon correcte aux prévisions de la théorie. L'insaturation ne concorde cependant pas avec la vitesse expérimentale

d'absorption de l'oxygène mais plutôt avec un nivellement apparent de la courbe d'absorption. Il semble de plus qu'un paramètre relié aux dimensions moléculaires, probablement les groupes terminaux du polymère, influence l'oxydabilité du polyéthylène.

### Zusammenfassung

Es wird gezeigt, dass bei der Untersuchung der Absorption von Sauerstoff durch Polyäthylen bei höheren Temperaturen durch Verwendung dünner metallischer Träger, deren Dicke die Tiefe der geschmolzenen Harzprobe festlegt, das zu Missständen führende Fließen des Polymeren vermieden werden kann. Der Einfluss der Zusammensetzung des Trägers auf die Reaktionsgeschwindigkeit wird für mehrere Metalle bestimmt. Die Reaktion der Sauerstoffabsorption zeigt bei Benützung von Trägern aus Monelmetall das klassische Verhalten gegen radikalische Inhibitoren und besitzt die gleiche Aktivierungsenergie, die für die Absorptionsreaktion ohne Träger charakteristisch ist. Bei Verwendung der Trägervorrichtung in einer vereinfachten, aus einer Trockenpistole nach Abderhalden hergestellten Gasabsorptionsapparatus für Sauerstoff, wird festgestellt, dass durch Methylverzweigung die Neigung zur Oxydierbarkeit des Harzes, wie zu erwarten, erhöht wird. Die Experimente liefern aber keine Beziehung zwischen dem ungesättigten Charakter und der Sauerstoffabsorptionsgeschwindigkeit, sondern eher eine solche zu einem offenbaren Abflachen der Absorptionskurve. Ausserdem ergibt sich, dass ein Parameter, der in Beziehung zur Molekulargrösse steht, wahrscheinlich die Endgruppen des Polymeren, Einfluss auf die Oxydierbarkeit des Polyäthylens hat.

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