The Mechanism of Polyethylene Oxidation*

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INTRODUCTION

It has long been known that paraffinic hydrocarbons are readily susceptible to thermal oxidation—and polyethylene is no exception to this general rule.
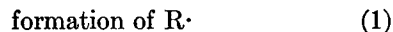
Since much of the processing of polyethylene involves exposure to air at elevated temperatures, there is ample opportunity for the material to oxidize. As this occurs, color, electrical and mechanical properties deteriorate. Such changes could greatly influence the processing and performance behavior of polyethylene and, therefore, limit its possible applications.

This paper deals with the mechanism of polyethylene oxidation, especially from the viewpoint of what is occurring during the oxidation induction period. This period is defined as the time interval in oxidation during which no physical changes and no apparent reaction occurs.
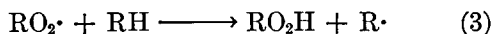
MECHANISM OF OXIDATION

In order to account for the autocatalytic nature of the initial stages of ethyl linoleate oxidation, Bolland[1] postulated a free radical mechanism. This mechanism,[2] which follows, has also been found to apply to low molecular weight hydrocarbons.
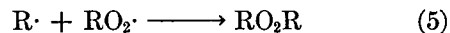
Initiation:

$$\text{formation of } R\cdot \tag{1}$$

Propagation:

$$R\cdot + O_2 \longrightarrow RO_2\cdot \tag{2}$$

$$RO_2\cdot + RH \longrightarrow RO_2H + R\cdot \tag{3}$$

Termination:

$$R\cdot + R\cdot \longrightarrow R-R \tag{4}$$

$$R\cdot + RO_2\cdot \longrightarrow RO_2R \tag{5}$$

$$2RO_2\cdot \longrightarrow RO_2R + O_2 \tag{6}$$

The first reaction, initiation, could occur by the breakdown of the hydroperoxide, RO_2H. This hydroperoxide can form either by direct air oxidation of an activated weak spot in the resin[3] or through propagation, e.g. (3). The latter effect, however, assumes more importance[2] as auto-oxidation proceeds. Equations (4) and (5) are not significant at the oxygen pressures used in this work.[1] As seen by consideration of the foregoing mechanism, oxidation is influenced by factors that catalyze peroxide decomposition. Such factors include ultraviolet radiation, and certain metals and metallic ions.

The abstraction of $H\cdot$ by $RO_2\cdot$ yields the initiating radical, $R\cdot$, which is the basis of autocatalysis in all hydrocarbon oxidation. Accordingly, the relative oxidizability of any hydrocarbon depends on the strength of the carbon-hydrogen bond. It is well substantiated in the literature[5] that a tertiary hydrogen is more susceptible to oxidation than a secondary hydrogen which, in turn, is more susceptible than a primary hydrogen. Also, adjacent double bonds[6] and carbonyl groups[7] tend to weaken the strength of the C—H bond, probably, primarily, as a result of the increased resonance stabilization of the $R\cdot$ radical formed.

Although branching, double bonds, or substitution of a carbonyl group in a hydrocarbon structure tend to accelerate oxidation, it must not be inferred that they are necessary. Saturated hydrocarbons[4] also yield hydroperoxide at an easily measurable rate.

EXPERIMENTAL

The general applicability of this autocatalytic mechanism to polyethylene has been pointed out by Biggs[9] and Wilson.[10] They determined the oxygen susceptibility of polyethylene by measuring
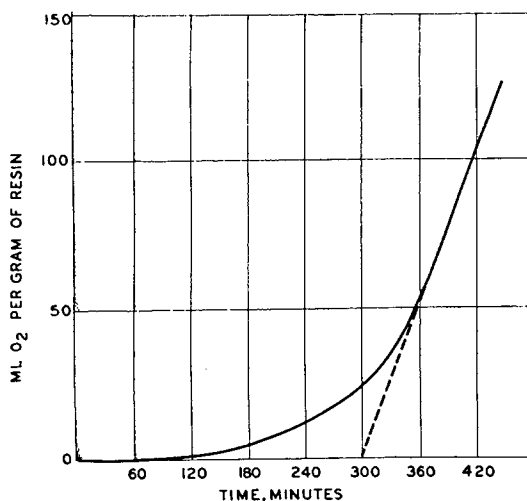
Fig. 1. Typical oxygen uptake curve for DYNH, 140°C.

volume pickup at constant temperature and pressure according to the method of Shelton;[8] one of their typical experimental curves is shown in Figure 1. The extrapolation of the straight line portion of the curve back to the x-axis gives the oxidation induction period.

In the present study, it was decided to measure, simultaneously, the products of oxidation as well as the length of the oxidation induction period. The setup used is shown diagrammatically in Figure 2. It basically consisted of an Erlenmeyer flask placed in an oil bath at 140°C., or any other specified temperature, and connected on one side to a receiving test tube, and on the other to an oxygen tank. Powdered polyethylene was dispersed on glass wool in the flask; and a thermometer was inserted in the gas inlet tube to within 1 in. of the flask bottom. In operation, oxygen is passed through the flask, and the volatiles are condensed in the test tube.

Temperature readings are taken at intervals until very rapid oxidation starts, and the temperature almost explosively rises to above 200°C. When bath temperatures lower than 130°C. are used,
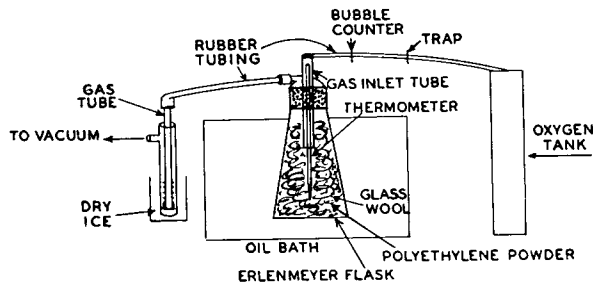
there is no temperature rise. Instead, the beginning of rapid oxidation is indicated by the appearance of water in the neck of the flask.
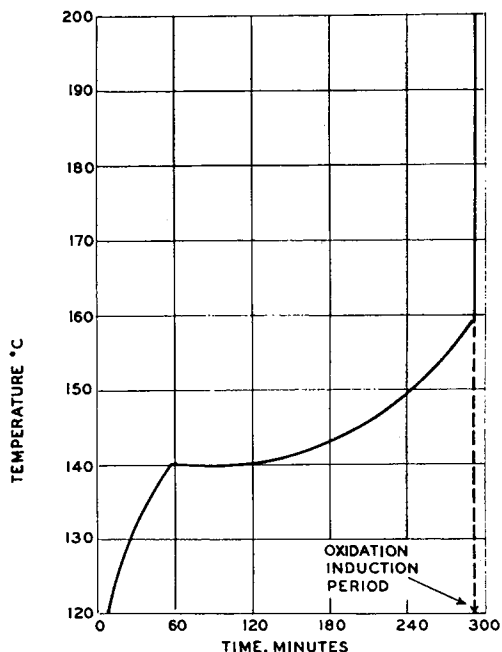

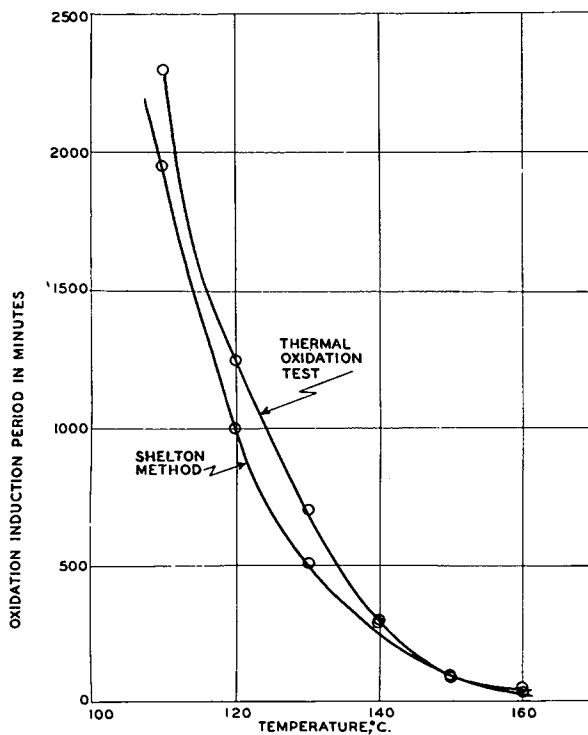
Fig. 3. Oxidation of polyethylene (average DYNH) at 140°C.

Fig. 2. Polyethylene thermal oxidation stability test.

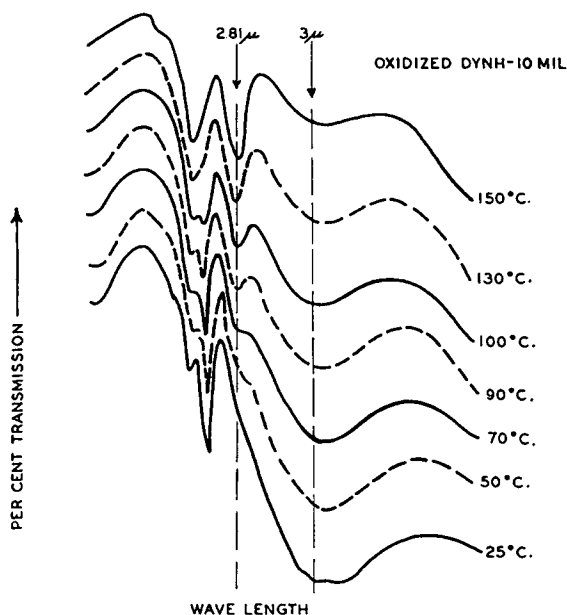Fig. 4. Oxidation induction periods for DYNH at 1 atmos. of O_2.

Fig. 5. Rate of formation of free and associated hydroperoxide vs. temperature.

Figure 3 shows a graph plotted from the test data. Here, the oxidation induction period is obtained by extrapolating from the point at which the temperature rises above 200°C. to the x-axis.

As seen in Figure 4, the oxidation induction periods by this thermal oxidation method are in general agreement with results obtained by oxygen pickup.[10]

The oxidation induction period provides a useful, indirect measure of the effect of oxidation on polyethylene resin. What is still needed, however, is some means of following the actual changes in structure during oxidation. Since all hydrocarbon oxidation by oxygen is considered to proceed via a hydroperoxide mechanism,[11] it is reasonable to look for the presence of hydroperoxides as an indication of incipient oxidation.

Rugg et al.[12] and Burnett et al[13] have shown that when polyethylene is oxidized, both free and associated hydroperoxide can be detected in the infrared. Free hydroperoxide appears at 2.81 μ, and the associated hydroperoxide at 3.00 μ. In experiments conducted by the Development Laboratories of Union Carbide Plastics Company, Division of Union Carbide Corporation, the late Mr. R. G. Fulton[14] followed the rate of formation of hydroperoxide on the hot stage of an infrared spectrograph. A 10-mil film of the sample being studied was placed on a hot sodium chloride plate, and the light passed through a lithium fluoride

prism. The concentration of free hydroperoxide was measured as a function of heating time at the 2.81 μ band. A band was also detected at 3.00 μ, indicating the presence of associated hydroperoxide. Figure 5 contains plots of transmissions at several temperatures of the free and associated hydroperoxides at 2.81 and 3.00 μ, respectively, formed when 10-mil films of DYNH are heated 1 hr. For the batch of Bakelite polyethylene DYNH observed, there is an equilibrium between the free and associated hydroperoxide at each temperature down to approximately 50°C., the free hydroperoxide disappearing at lower temperatures.

This infrared method can only serve as a qualitative analytical tool, however, since the 3.00 μ band is uncalibrated and consists of unknown amounts of associated peroxide, hydroxyl and, perhaps, other structures.

In addition to hydroperoxide content, several other resin properties were measured. The carbonyl content, for example, was determined on pressed films at the 5.85 μ absorption band in the infrared. The absorption coefficient used in the calculation of the concentration was taken to be the average of the measured coefficients for several compounds of known structure. Melt index was determined according to ASTM D1238–52T, specific gravity by ASTM D1505–57T, tensile and elongation by ASTM D412–51T, and power factor by ASTM D150–54T.

DISCUSSION

The Oxidation Induction Period

The oxidation induction period is understandable in terms of a peroxide mechanism. As measured on the hot stage of an infrared spectrograph, hydroperoxide forms and quickly reaches an equilibrium concentration where the rates of formation and decomposition are equal (Fig. 6). Thus, hydroperoxide appears as one of the first products of oxidation. Kinetic studies[15] have shown that subsequent oxidation is autocatalyzed by the decomposition of hydroperoxide to free radicals.

Figure 7 is a plot of the formation of carbonyl absorbance/mil vs. time; the data were obtained when a 10-mil film of DYNH was heated in air on the hot stage of an infrared spectrograph. Both in air on the hot stage and on heating in oxygen at 140°C., as in the thermal oxidation method, carbonyl formation goes through an autocatalytic stage during which the rate of formation is increasing. The carbonyl then reaches a steady-state
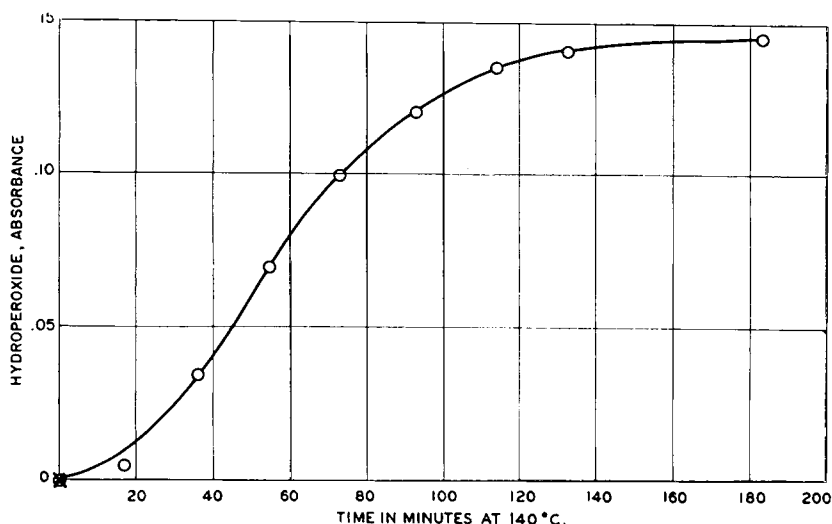
Fig. 6. Concentration of hydroperoxide vs. time at 140°C. in DYNH, based on 2.81μ absorption band.

rate. For example, when DYNH resin was heated in oxygen at 140°C., this steady-state rate was constant for the 5-hr. period up to the explosive combustion, which signifies the end of the oxidation induction period.

Peroxide formation has been shown to occur long before the end of the oxidation induction period. This period seems to be the time necessary for the buildup of sufficient peroxides and their free radical decomposition products to cause a rapid oxidation. It is not, as was verified by extensive purification, the time necessary to use up a natural antioxidant.

In view of the reactions occurring during the oxidation induction period, it can readily be shown that oxidation is a cumulative effect and that the more a resin has been oxidized, the more easily it is further oxidized. In an experiment, two samples of DYNH were oxidized at 140°C. in an oxygen atmosphere for 1 and 2 hr.; under these conditions

polyethylene has an oxidation induction period of 5 hr. When these partially oxidized resins were further oxidized under the same conditions two weeks later, their oxidation induction periods were correspondingly reduced.

Table I shows the effect of progressive oxidation on weight-% carbonyl, melt index, and density. The increasing melt index reveals the chain scission caused by oxidation. The true meaning of the expression "the end of the oxidation induction period" is shown by the tremendous rise in melt index, carbonyl, and density. This rise is indicative of the start of *very* rapid oxidation.

TABLE I
Effect of Oxidation on Bakelite Polyethylene Resin DYNH

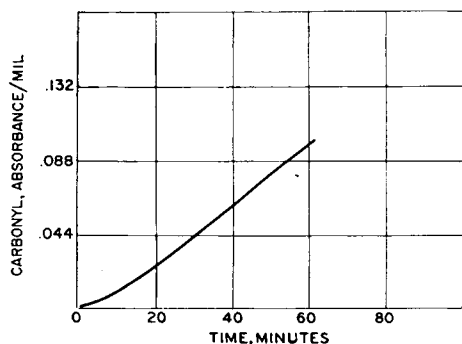| Time in min. at 140 °C. in oxygen	Melt index	Carbonyl, wt.-%	Specific gravity
0	2.0	0.001	0.917
45	3.0	0.030	0.920
90	3.8	0.060	0.921
280	33.1	Very large	0.932

Fig. 7. Weight-% carbonyl in DYNH resin vs. time in air at 140°C.

Other physical changes occurring during oxidation were revealed when a 20-mil plaque of DYNH was exposed to oxygen at 100°C. The color deepened and tensile strength and elongation decreased (Table II). At any temperature some crosslinking occurred simultaneously with chain scission, as was evidenced by toluene insolubles.

TABLE II
Effect of Oxidation on a 20-Mil Plaque of Bakelite Poly-
ethylene Resin DYNH-9, 7282

wt.-% carbonyl,	Color	Tensile strength	% elongation
0	Colorless	2350	640
0.15	Very light yellow	1800	590
0.50	Dark Yellow	900	40

Infrared analysis[14] of lightly degraded (0.15% carbonyl) resin indicated primarily ketonic carbonyl with a small concentration of aldehyde and acid carbonyl. As oxidation proceeded, alkali solubility showed that the concentration of acid carbonyl increased. Analysis (ultraviolet, infrared, and mass spectrometric) of the volatiles revealed the presence of short-chain ketones, aldehydes, acids, hydrocarbon unsaturates, water, and carbon dioxide. These products arise as a secondary result of peroxide decomposition, the first result being free radical formation. In the Bolland mechanism, RO_2R is formed in termination. When RO_2R decomposes, the first product formed is $RO\cdot$ and this in turn, according to Vaughan,[16] can lead to many other products such as alcohols, aldehydes, ketones, and acids.

Variables Affecting Oxidation Rate

What are the factors which affect the rate of polyethylene oxidation and the length of the oxidation induction period? The most obvious factor is temperature. The higher the temperature, the greater the rate of oxidation and the shorter the oxidation induction period (see Fig. 1). It has also been shown that the extent of previous oxidation is critical. The higher the peroxide content of a resin, the shorter the induction period.

Other factors which affect the rate of oxidation are unsaturation and branching.[17] The first three resins shown in Table III have both high branching and high unsaturation compared with an average lot of DYNH. They also have poor oxidation stability. Although it would appear from the data that resin stability may vary with molecular weight as well as with unsaturation and branching, subsequent experiments (described below) tend to refute this theory.

The data in Table IV clearly indicate that molecular weight variations do not affect the rate of oxidation, at least in the range covered. Bakelite†

† Registered trade-mark of Union Carbide Corporation.

TABLE III
The Effect of Unsaturation and Branching on the Oxidation
Stability of Bakelite Polyethylene resins

Resin	Approximate[a] molecular weight	Oxidation induction period, min.	Unsatura-tion, total, wt.-%	Degree of branch-ing, % methyl
DYDT	4,000	150	0.33	10
DYGT	7,000	170	0.30	—
DYLT	12,000	225	0.27	—
DYNH	21,000	280±30	0.10	3
DYNK	24,000	275	0.09	—

[a] Viscosity average.

polyethylene resin DMH-50 was prepared by thermal degradation of DYNH in an inert atmosphere. A comparison of DMH-50 with Bakelite polyethylene resin DYDT shows that both have approximately the same molecular weight and degree of unsaturation, but DYDT has far more branching. DYDT has a much shorter oxidation induction period than DMH-50, indicating the deleterious effect of branching on oxidation stability. DMH-50 has the same branch content as DYNH but is of very much lower molecular weight and has a somewhat higher percentage of double bonds. Its induction period is within experimental

TABLE IV
Effect of Molecular Weight and Branching on Oxidation
Stability

Bake-lite poly-ethyl-ene resin	Oxidation induction min.	Molecular weight	Total unsatura-tion, wt.-%	Degree of branch-ing, % methyl
DYDT	150	4,000	0.33	10
DMH-50[a]	250	3,000	0.40	3
DYNH	280±30	21,000	0.10	3

[a] Prepared by F. P. Reding, Union Carbide Corporation.

error of that of DYNH. A better distinction between the variables of molecular weight and unsaturation is made in the next section.

Hydrocarbon Prototypes

It is often difficult to assess the relative effect of various structural factors in polyethylene on the oxidation induction periods because of the many variables involved. Therefore, pure hydrocarbons of known structure were studied by the thermal

oxidation test method. Three were straight chain hydrocarbons with increasing molecular weight, the fourth was a ketone, and the fifth an unsaturated hydrocarbon. As Table V demonstrates, molecular weight does not affect stability. However, both the ketone group and the double bond produce a dramatic decrease in the oxidation induction period.

TABLE V
Hydrocarbon Structure vs. Oxidation Stability

Hydrocarbon	Oxidation induction period, min.
Octadecane	240
Eicosane	245
Dotriacontane	230
Laurone	65
17-Pentatriacontene	60

Low-Temperature Aging of Polyethylene

The oxidation of polyethylene has been studied at reasonably high temperatures to simulate processing conditions. But, it might well be asked: Are the conclusions reached during high-temperature oxidation also valid at lower temperatures?

that at low temperatures, as at high temperatures, unsaturation and branching accelerate oxidation.

Effect of Irradiation on Oxidation Rate

Evidence has been presented that branching accelerates oxidation. The possibility of further evidence for attack at tertiary hydrogens is afforded by a study of polyethylene irradiated in air. That the irradiated test resins were badly oxidized was proven by their rank odor. However, their oxidation stability was not reduced. It could be surmised that the radiation-produced crosslinking had somehow stabilized the resin against oxidation degradation. If the crosslinking reaction occurred between tertiary carbons via the evolution of tertiary hydrogens, this apparent stabilization would seem reasonable.

Metal-Catalyzed Oxidation

All the experiments and data described up to this point have shown what happens to DYNH during oxidation. The next logical question was: Is the course of this oxidation changed by the presence of metal? Two sets of experiments were devised to provide an answer; the first set was concerned with reaction products.
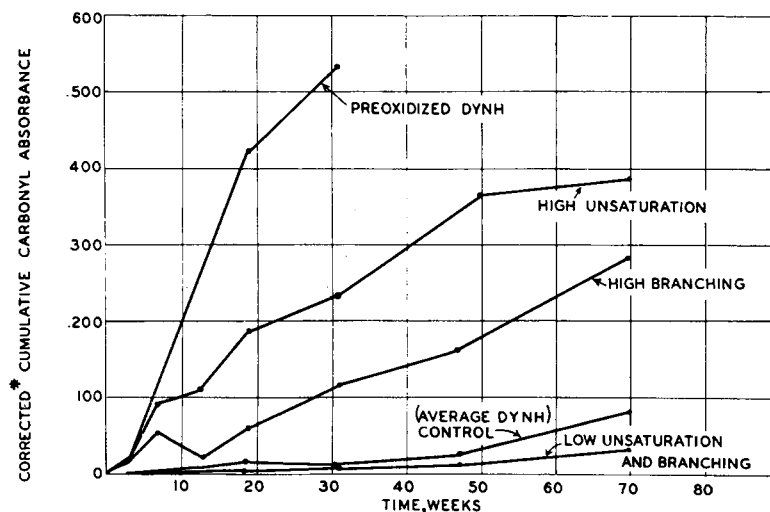

Fig. 8. Rate of carbonyl formation (absorbance/mil) at 60°C. in polyethylene.
(*Carbonyl absorbance at any time minus the initial carbonyl absorbance.)

A number of 20-mil compression molded plaques were heated at 60°C. and analyzed for rate of carbonyl formation. The samples chosen were representative of the various structural characteristics of the resin. The data plotted in Figure 8 reveal

One per cent manganese dioxide was milled into DYNH on a two-roll mill set at 110°C. Ten-mil plaques were compression molded from this material, and then heated at 60°C. for 6 months in a closed container. The original material was

black. After the heating period, the material was white. On vacuum distillation, three fractions were obtained, which were then subjected to infrared analysis.[15] The first was an oily, colorless, highly volatile liquid, probably consisting of a mixture of low molecular weight acids, aldehydes, alcohols, and possibly esters. The second fraction was a yellow, soft solid—similar in composition to the first fraction, but of longer chain length. Alcohols were absent. Both of these fractions were present in very small amounts.

The third fraction, which was by far the major component, was the residue in the pot. This product no longer resembled polyethylene. It was a completely unbranched, oxidized hydrocarbon mixture probably consisting of acids and esters of about 30 carbons in length. Unsaturation had also considerably decreased.

The second set of experiments was designed to determine if any rate change occurred in the presence of metal. To answer this, several resins of different structure were pigmented with manganese dioxide and heated at 60°C. in air, and the rate of carbonyl formation was determined. These test resins were the same as those used to obtain low-temperature aging properties of polyethylene (see Fig. 8). Branching, unsaturation, and preoxidation have the same general effect during metal-catalyzed oxidation as during nonmetal-catalyzed oxidation. Each rate, however, was greatly accelerated in the presence of metals.

The Role of Antioxidants

Although unsaturation and branching accelerate oxidation, straight-chain saturated hydrocarbons and straight-chain saturated polyethylene resins also oxidize at a measurable rate. Therefore, the addition of an antioxidant is the only practical means of protecting polyethylene against oxidation. Antioxidants have long been used to protect rubber and other polymers[18] from oxidation. An antioxidant serves to terminate the normal oxidative chain reaction by forming either a nonradical species or radicals of very low reactivity.

Using 0.02% 2,6-di-t-butyl 4-methyl phenol (DBPC), the oxidation induction period, for example, was greater than 10 hr. compared to $4^1/_2$ hr. for unstabilized DYNH. Yet, as can be seen in Figure 9, 0.02% DBPC gave only a 60-min. induction period in the formation of hydroperoxide. Thus, reaction occurs during the induction period even in the presence of antioxidant.
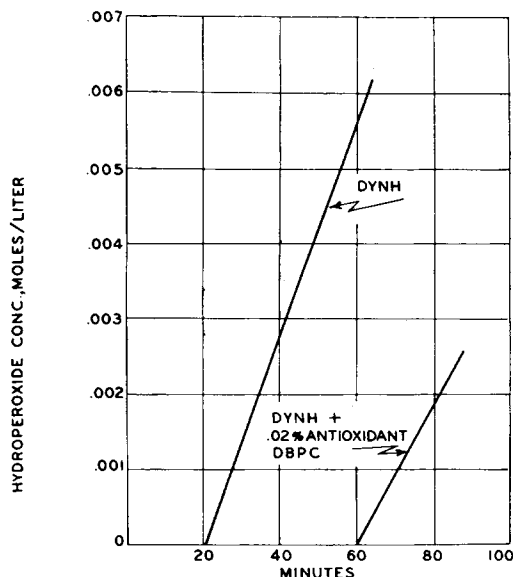
The reactions occurring during the induction

Fig. 9. Rate of formation of hydroperoxide in polyethylene at 140°C., through infrared analysis.

period, however, do not cause a change in gross physical properties. The small changes which do occur are insignificant for most uses.

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Synopsis

As evidenced by formation of peroxides and carbonyl, reaction occurs during the oxidation induction period of polyethylene. The meaning of the term oxidation induction period is revealed by the tremendous change in melt index, carbonyl, density, color, tensile, and elongation occurring towards the end of this time period. Hydroperoxide forms long before the end of the oxidation induction period even in the presence of an antioxidant. At any temperature both chain scission and crosslinking occur simultaneously. The rate of oxidation is accelerated by increasing temperature, unsaturation, and branching. Molecular weight seems to have no effect.

Résumé

Comme on l'a mis en évidence par la formation de peroxydes et de groupes carbonyles, la réaction se passe durant la période d'induction d'oxydation du polyéthylène. Le sens du terme période d'induction d'oxydation est révélé par le changement énorme de l'indice de fusion, de la teneur en groupe carbonyle, de la densité, de couleur, d'extensibilité et d'élongation se produisant vers la fin de cette période. L'hydroperoxyde est formé longtemps avant la fin de la période d'induction d'oxydation même en présence d'un antioxydant. A n'importe quelle température la rupture de chaîne et le pontage se produisent simultanément. La vitesse d'oxydation est accélérée par augmentation de la température, de l'insaturation et de la ramification. Le poids moléculaire semble n'avoir aucun effet.

Zusammenfassung

Wie die Bildung von Peroxyden und Karbonylgruppen beweist, treten schon während der Induktionsperiode bei der Oxydation von Polyäthylen Reaktionen auf. Der Ausdruck Induktionsperiode bedeutet bei der Oxydation, dass gegen das Ende dieses Zeitabschnittes eine gewaltige Änderung des Schmelzindex, des Karbonylgehaltes, der Dichte, der Farbe, der Festigkeit und Dehnung auftritt. Hydroperoxyd entsteht sogar in Gegenwart eines Antioxydans lange vor dem Ende der Oxydations-Induktionsperiode. Bei allen Temperaturen treten zur gleichen Zeit Kettenspaltung und Vernetzung auf. Die Oxydationsgeschwindigkeit wird durch höhere Temperatur, durch den ungesättigten Charakter und durch Verzweigung hinaufgesetzt. Das Molekulargewicht scheint keinen Einfluss zu haben.