Assay of Polyethylene Oxidizability by Lead Peroxide Ignition*

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INTRODUCTION

The current annual production rate of polyethylenes is close to one and one-half billion pounds per year. The conversion of this enormous production to articles of commerce involves heat treatments designed to enhance the resin's plasticity and, hence, its formability. As a hydrocarbon, polyethylene is oxidizable, especially when hot. However, reaction occurs, albeit at a more leisurely pace, even at ordinary temperatures. It proceeds with enhanced rapidity when exposed to the catalytic action of light. This underlies the phenomenon of the plastic's aging. Given the ubiquity of oxygen, the quality of resin-oxidizability translates into a factor of some economical and technical significance. It becomes important to know the differences in the oxidizability of polyethylene resins and to understand the reasons for these differences.

Because the enthusiasm of oxygen for the polyethylenes elicits practical concern, much effort has been expended in its study. Mesrobian and Tobolsky[1] and Biggs and Hawkins[2] have explored the effects in classic papers, and more recent work has added important details to our understanding of the reaction.[3-5] Yet, despite its intensive study, this reaction is seldom used in assessing the oxidative differences between polyethylenes,[5] and it is employed only haltingly in assaying the efficacies of antioxidants used to protect polyethylenes, despite its intensive development in many laboratories for this specific purpose. The reasons stem from the complexity of the reaction, its extreme sensitivity to extraneous influences, and the interference with its course by its very reaction products.

The study of the relative oxidizability of various polyethylenes stands in need of a more suitable technique. The intent of this paper is to present such a tool and to illustrate its utility for differentiating among polyethylene resins.

PRINCIPLE

The technique involves a solid–solid oxidation reaction.   It is, in effect, a dry redox system that reacts at elevated temperatures, resulting in ignition. While not too usual, dry redox systems are hardly new; some have been the subject of careful study,[6] others have had a most profound influence on the course of history and, indeed, are charged with the heavy burden of knighthood's demise.[7]

The system is comprised of a powdered mixture of lead peroxide as oxidant and of polyethylene resin as reductant.   A standard mixture of these components, exposed in a standard manner to elevated temperatures, usually of 230 to 280°C., on the surface of a hot plate, ignites after a time interval which is a function of the temperature and of the particular polyethylene being tested.   The time interval to ignition, designated as ignition time, is measured in hundredths of a minute and is of less than one minute's duration.   By varying the ignition temperature, inverse variations are obtained in ignition time.   The plotting on semilog paper of ignition temperatures versus ignition times, with ignition time on the log coordinate, yields, for the significant portion of its reaches, a straight line.   Curves for
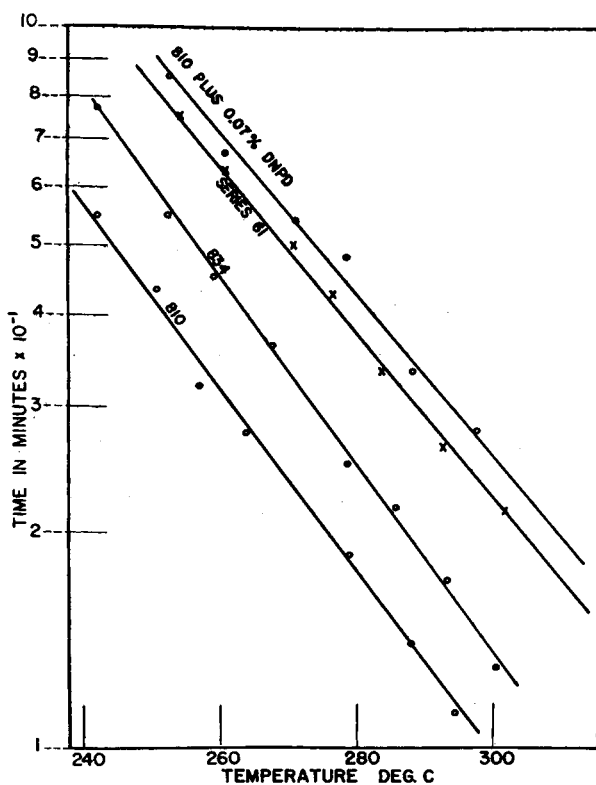

Fig. 1. Differentiation among Tenite polyethylenes by lead peroxide ignition.
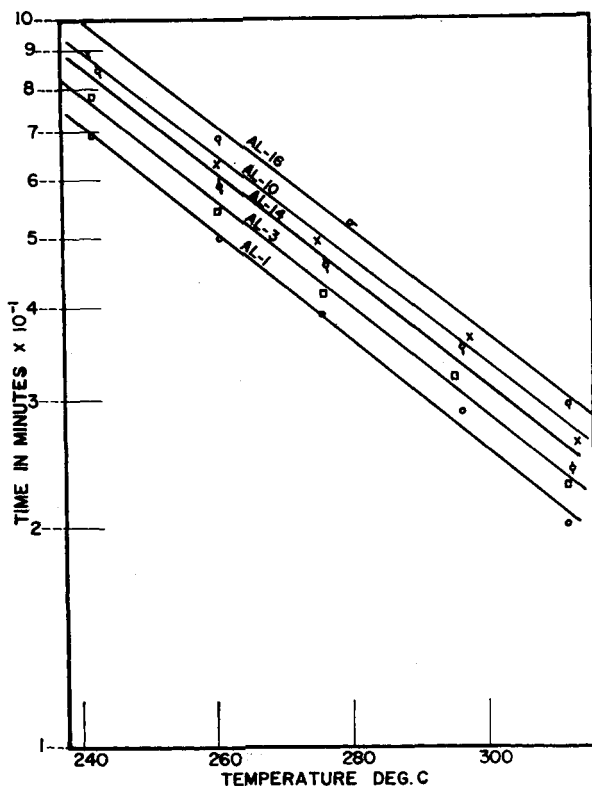
Fig. 2. Differentiation among Alathon polyethylenes by lead peroxide ignition.

different polyethylenes, representing reactions of an invariant oxidant (PbO₂), and different reductants (the different polyethylenes), reflect differences in the reducing power or oxidizability of the polyethylene resins being tested. Typical differences found for polyethylenes are shown, for various Tenite resins, in Figure 1. In these curves, the resins showing the higher intercepts with the time axis, that is, those which take longer to ignite, are the more resistant to oxidation. Figures 2 and 3 illustrate differences among certain of the polyethylenes produced by Du Pont and Union Carbide, respectively.

EXPERIMENTAL

Standardization

The experimental parameters that influence the results of the procedure are those common to heterogeneous solid–solid reactions, and include sample size, particle size, degree of sample compression, and intimacy of hot plate contact. The experimental approach consists of arbitrarily standardizing those factors found to be pertinent to the attainment of
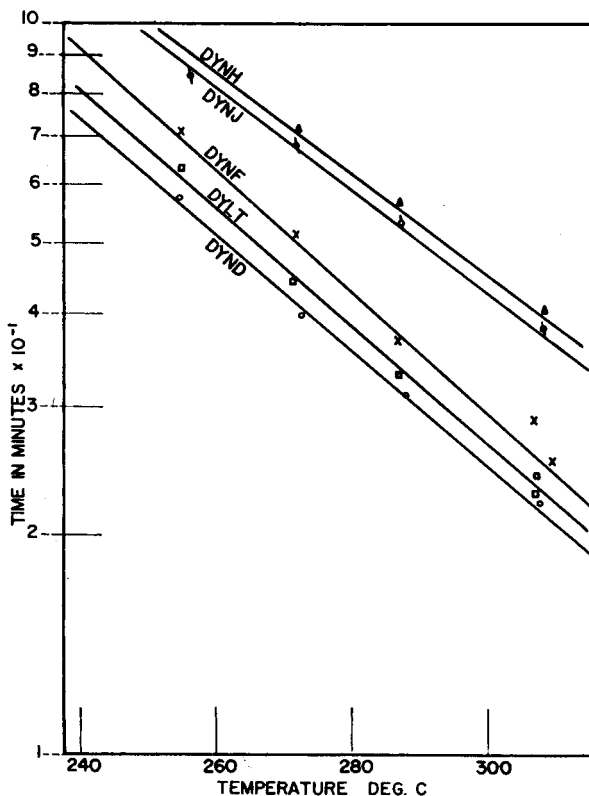
Fig. 3. Differentiation among Union Carbide polyethylenes by lead peroxide ignition.

acceptable precision. The result is an empirically standardized experimental procedure suitable for obtaining relative values for the resins examined.

Sample Size and Disposition

The testing procedure involves the placing of a small sample of lead peroxide–resin mixture upon the heated surfaces of a hot plate. Standardization of sample size is achieved by the use of a scoop having an arbitrary capacity of 0.2 g. The scoop is constructed of 6-mm. ID glass or metal tubing having a cylindrical height of 6 cm. Perhaps the most important parameter governing the precision of ignition times is the general geometric arrangement of the sample upon the hot plate surface, especially in respect to the degree of scatter and compactness. Standardization of this arrangement is effected by the use of a funnel, the tip of which is clamped $1^1/_4$ in. above the hot plate surface. The Pyrex filter funnel is 65 mm. in diameter and has a straight cut stem of $2^1/_4$ in. in length. During the progress of the test, the stem of this funnel, through which the sample is directed onto the

hot plate's surface, is cleaned as required, by the abrasive action of a pipe cleaner.

Attempts were made to use a pelletized sample as a means of standardizing its deposition upon the hot plate, but the method offered no advantages in terms of experimental precision.

Hot Plate

Results reported in this paper were all obtained on a 6 × 6 in. Temco hot plate Model 1900 operating on 115 v. The important factor of reproducibility of contact between the sample and hot plate surface was enhanced by smoothing the face of the hot plate with No. 150 emery cloth. After each ignition the reaction debris was brushed away, and the surface was cleaned with a piece of similar cloth. Temperature regulation was made more precise by reliance on a Variac control rather than on the bimetallic control switch integral to the hot plate. The accurate recording of hot plate surface temperature is, of course, essential to this procedure. This is managed by the use of a thermocouple wire held firmly against the hot plate surface by the pressure transmitted, through a Teflon collar of about $1/6$ in. thickness, by the shoulder of a set screw which fastens into a hole drilled and tapped into the hot plate surface. The sample whose ignition time is to be measured is directed onto the hot plate surface within $1/2$ in. of the location of the set screw and thermocouple wire. The heat source in this hot plate consists of a square unit of about $1 1/4$ in. on edge, located immediately below the face plate. The center of the heating element is located midway from the sides of the plate but is displaced $3/8$ in. rearward from the center of the face plate. It follows from the design
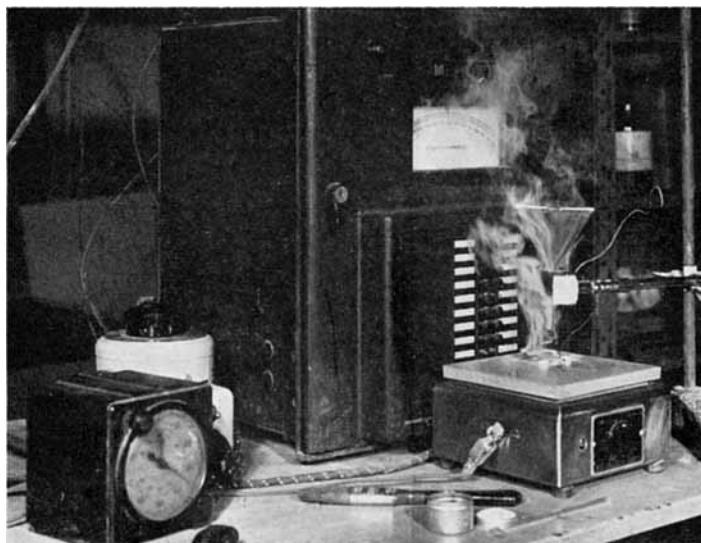

Fig. 4. Attachments used in securing thermocouple wire. Note position of ignition area relative to tip of funnel.

of this hot plate that there is a temperature gradient from the heating square to the edges of the face plate, and that this gradient must manifest itself even across the small distance separating the thermocouple lead from sample ignition point. In actual point of fact, the location of the thermocouple at a point immediately over the center of the heating square gives a temperature which, for the ranges required by this test procedure, differs at
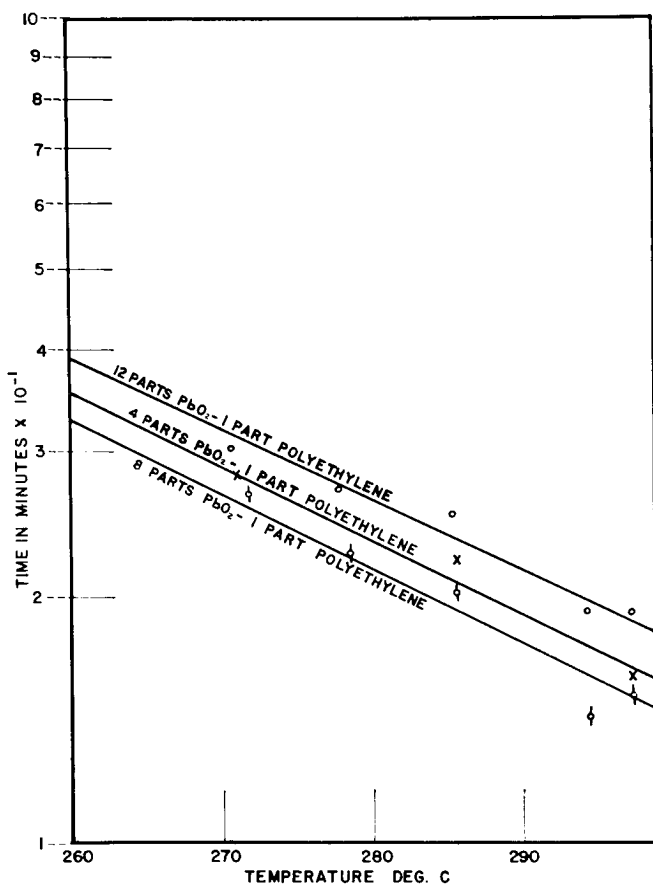

Fig. 5. Effect of reactant ratio on ignition characteristics; using DYNF through 80 mesh.

the most by only 2°C. from a spot located $1\frac{1}{2}$ in. closer to the nearest edge. The point chosen for ignition of the samples is between both points. The error between the true temperature of the ignition point and that recorded by a single thermocouple point would, at the most, be less than 2°C. At the temperature ranges employed, this falls within the three one hundredths of a minute accepted as the precision of the ignition-time test results. Figure 4 illustrates the attachments used to secure the thermocouple wire, and shows the position of the ignition area relative to the tip of the funnel.
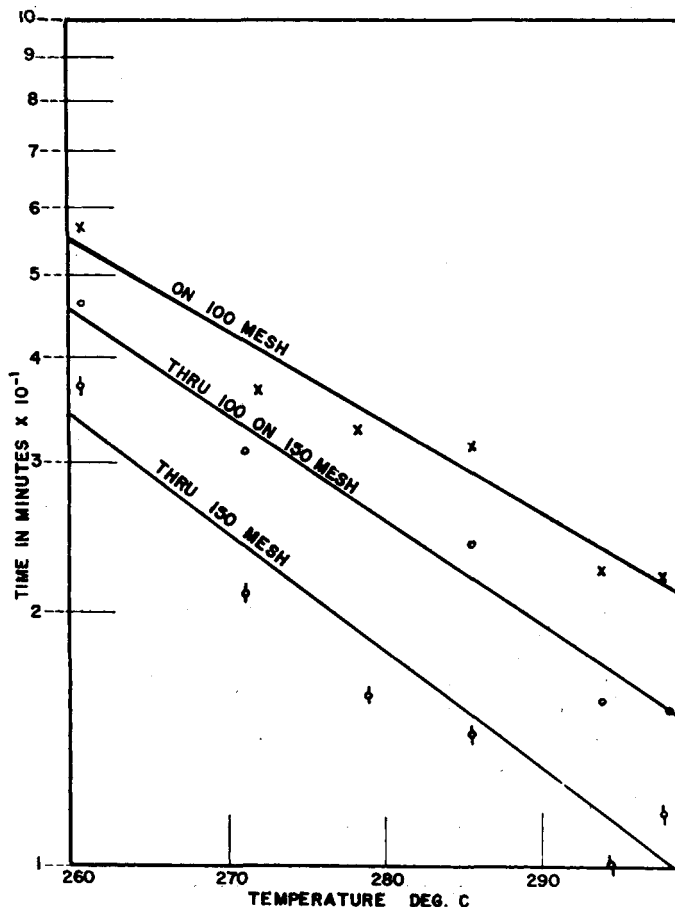
Fig. 6. Effect of polyethylene particle size on ignition characteristics using DYNF 8:1 mix.

Composition of Redox Mix

Different ratios of lead peroxide and a given polyethylene were found to give different ignition time values. This is shown for DYNF resin in Figure 5. A ratio of 8 parts lead peroxide to 1 part polyethylene was arbitrarily selected as the standard mix.

As might have been expected, the finer the particulation of the polymer comprising the standard mix, the faster its ignition. This is illustrated in Figure 6. Since the finer resin particles are not too plentifully produced in the grinding process, the particle size selected for use in the standard mix was mesh −60 + 80. Grinding of the polyethylenes is best performed with a device which minimizes heat build-up, else fusion of the resin particles results. Wiley mills are suitable for this purpose, since they rely for their action on the shearing effect of moving blades. However, the grinding of

polyethylenes under liquid nitrogen (a service obtainable from the Liquid Nitrogen Processing Corporation, Malvern, Pa.) is to be preferred[8] because, being done at temperatures far below the glass temperature of all polyethylenes, it is less likely to yield particles of different shapes from polyethylenes of different melting points.

Procedure

The lead peroxide used was Merck's reagent grade. Although its particle size did not seem to influence ignition time, it was sieved through 200 mesh cloth, to break up agglomerates. The standard mix was then prepared by blending the peroxide with polyethylene resin of the standard mesh size by three passes through a 40 mesh screen.

A standard scoopful of the mix was dropped through the funnel onto the hot plate whose temperature had been observed to hold constant for 1 hr. The time to ignition was then noted. When comparisons were being made among resins, they were all tested at the same temperature, then the temperature was altered to a second level. Three readings were made at each temperature for each resin. The target precision was ±0.03 min. When precision was not achieved within the first three readings, a fourth was taken. Depending upon the scatter of the reading, all were averaged, or the single (usually) disparate one was discarded. The results were plotted with five temperature points so selected as to give ignition times of not less than 0.10 nor more than 1.00 min. Results thus obtained are presented in Figures 1–3.

OXIDATIVE BASIS OF TEST

During the course of the ignition, lead peroxide is reduced to lead oxide. Since the only other component of the reaction mixture is polyethylene, it follows that in the ignition reaction polyethylene is oxidized by the peroxide. Because the only chemical variant in the different formulations is the different polyethylene, it seems logical to conclude that the differences in reaction time reflect differences in the ability of the polyethylenes to react oxidatively with the lead peroxide. Moreover, there are experimental augmentations to this chemical logic which directly relate the fate of polyethylenes in this test to that which befalls them in their classic reaction with oxygen gas at elevated temperatures.

The shielding effect that antioxidants exert for polyethylenes against assault by oxygen is well known. Figure 7 indicates that precisely that same influence is wielded by the same antioxidants in protecting polyethylenes against ignition by lead peroxide. The antioxidative protection is manifested in this test by the need to increase the reaction temperature in order to get a given rate of reaction (ignition time) in the presence of antioxidant. This is shown to hold true for resins of the same base protected by incrementally larger quantities of antioxidant.
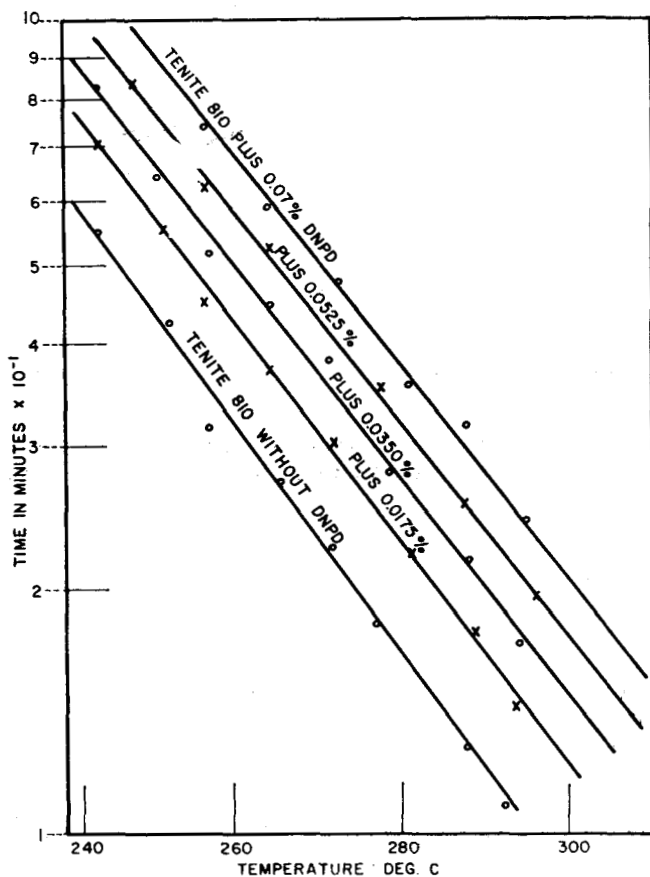
Fig. 7. Effect of using Tenite 810 with DNPD; incremental variations of 0.0175% on ignition characteristics.

The countereffect of oxidation acceleration by metallic compounds[9] is demonstrated in a parallel manner for both the oxygen uptake and lead peroxide ignition reactions. Four samples of a polyethylene resin were examined. One of these represented a base DYNK resin. The second was this same resin milled for 1 min. The third and fourth samples represented this base resin milled for 1 min. each with one of two coloring substances of the copper phthalocyanine type. Figure 8 shows that differentiation is obtained among these samples by the use of the lead peroxide ignition test. A similar differentiation is shown by the specific viscosity values of these samples and by the tensile and elongation values of these materials in the form of ASTM tensile bars following oxygen bomb aging.[10] This is illustrated by Table I.

That branching in polymeric materials predisposes them to oxidation by creating tertiary hydrogen atoms is well established. Experimental confirmation of the direct influence of extent of molecular branching on poly-
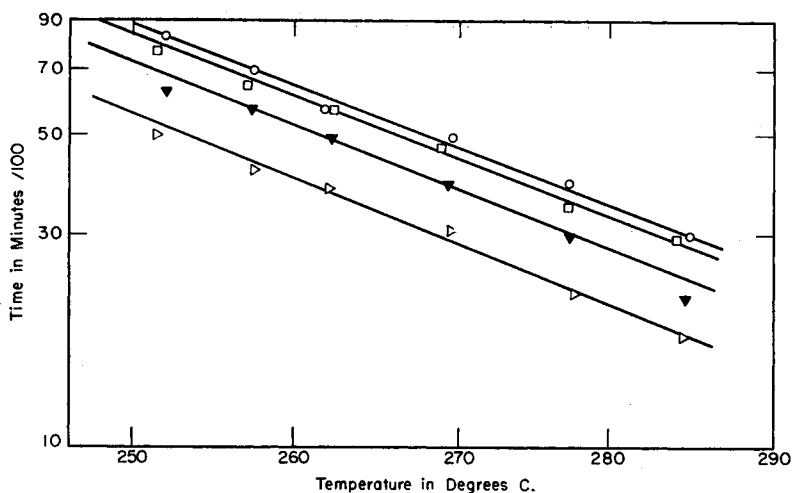
Fig. 8. Effect of copper phthalocyanine dyes on ignition characteristics using DE-2450 resin: (O) unmilled; (□) milled; (▼) with 1% Monastral Green; (△) with 1% ultramarine blue.
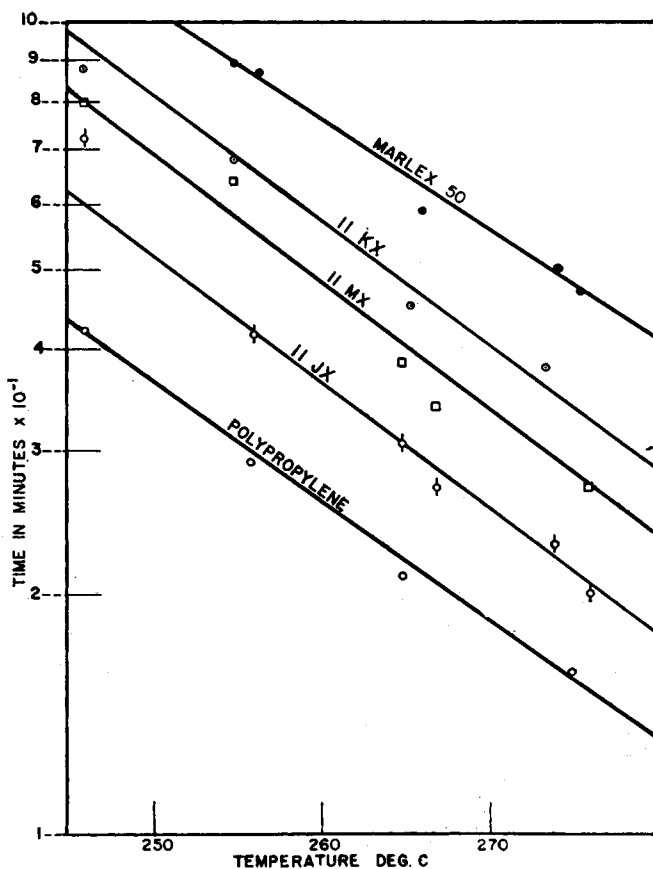

Fig. 9. Lead peroxide ignition test, effect of methyl branching. Methyl groups per 1000 carbon atoms: Marlex 50, 1.0; 11 KX, 10.7; 11 MX, 21.0; 11 JX, 35.5; polypropylene, 333.

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TABLE I
Effect of Organometallic Dyes on Oxidative Degradation

Code	Resin	Treatment	Pigment	Unaged		Aged in bomb at 80°C. for 14 days at 300 psi O_2		
				Stress, psi	Elong., %	Stress, psi	Elong., %	Sp. visc.
A	DYNK	Unmilled	None	1820	178	1245	34	0.477
B	DYNK	Milled 1 min. at 270°F.	None	1760	187	1125	16	0.470
C	DYNK	Same as B	1% Monastral Green CT-674-D	1720	192	690	6	0.467
D	DYNK	Same as B	1% ultramarine blue UB 6130	1710	154	Samples very brittle and broke during handling		0.437

ethylene oxidizability has been presented for the reaction of oxygen gas with the polymer[5] and also for the oxidative effect of fuming nitric acid on the resin.[11]   Exactly the same influence is seen to operate in the lead peroxide ignition reaction.   Thus, Figure 9 shows that a linear polyethylene is less easily ignited with lead peroxide than is a polypropylene resin (highly branched), and that three ethylene–propylene copolymers having intermediate amounts of branching ignite with an ease proportionate to their extent of branching.

The suitability of the lead peroxide ignition test for assessing the oxidation resistance of polyethylenes is thus seen to depend upon the identity of effects exhibited by both oxidation inhibitors and accelerators in this reaction and in the oxygen gas reaction.   In addition, there is the identity of effect of chain branching in both reactions.

TEST CHARACTERISTICS

Stability of Redox Mix

The standard mixes of lead peroxide and polyethylenes are completely stable when stored at room temperature for as long as three years, measured by analysis for peroxide content and ignition time values.   Storage at 50°C. caused no changes in these values over a period of at least one month. Oven storage at 100°C. resulted in changes in peroxide content as well as in ignition times after nine hours.   From the above, it is evident that stand-
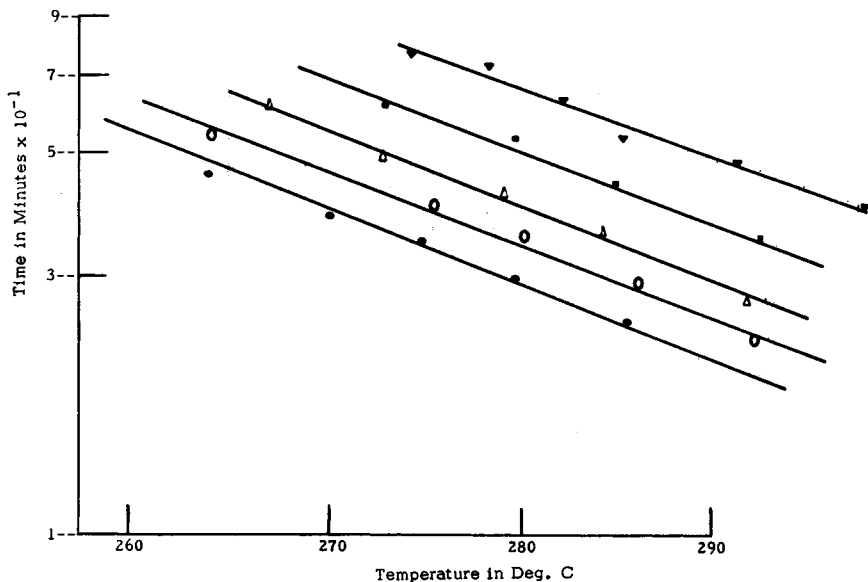

Fig. 10. Nontriggering effect.   Resin composition: (▼) 100% Alathon (Al.) 20; (■) 75% Al. 20 + 25% Al. 14; (△) 50% Al. 20 + 50% Al. 14; (O) 25% Al. 20 +.75% Al. 14; (●) 100% Al. 14.

ard mixes remain unreacted and can be retained as trustworthy references, provided they be stored at room temperature.

Nontriggering Effect

As indicated above, the additions of even small quantities of oxidation inhibitors or accelerators to polyethylenes exert influence on the resins' ignition time values. Therefore, investigations were undertaken to ascertain whether a polyethylene admixed with a small quantity of a second resin having a lower ignition point would be triggered into premature reaction with lead peroxide. Figure 10 shows that this is not the case. Mixtures of polyethylenes having different ignition values respond to this test on an average-concentration basis. Premature ignition of one polyethylene triggered by the presence of a second does not occur.

Effect of Carbon Black Filler

The presence of carbon black milled into the polyethylenes delays the onset of ignition. This possibly follows from the carbon black's serving as a diluent to separate and, hence, to insulate from one another particles of the redox components. Alternatively, this effect may arise from carbon black's known antioxidative property.[12] In any case, the effect is shown in Figure 11, wherein the presence of increasing percentages of carbon black is seen to have a progressively greater influence in postponing the occurrence of ignition.
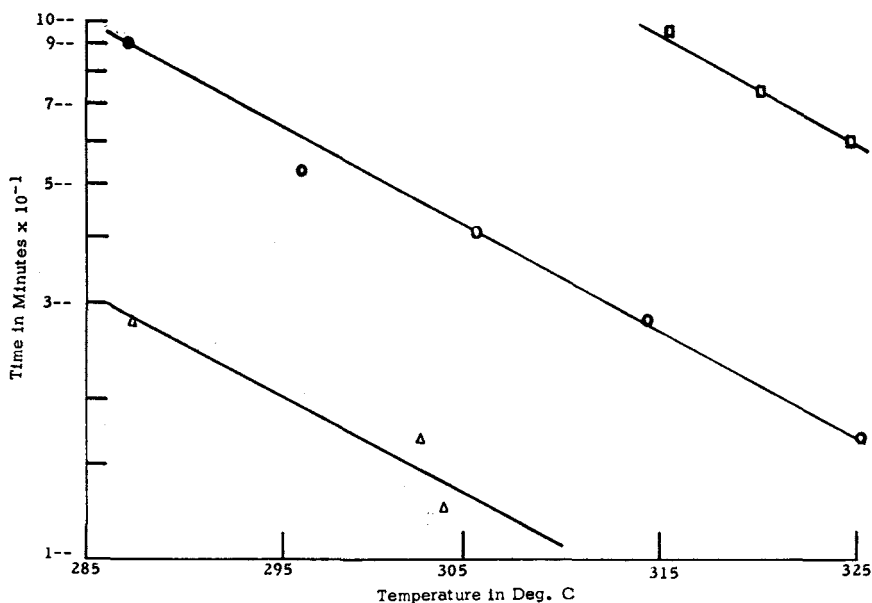

Fig. 11. Effect of carbon loadings on ignition characteristics, using DYNK resin. Per cent carbon: (△) zero; (O) 10; (□) 25.

UTILITY OF METHOD

As already stated, this method is capable of differentiating among polyethylene resins on an oxidizability basis. It can, therefore, be employed
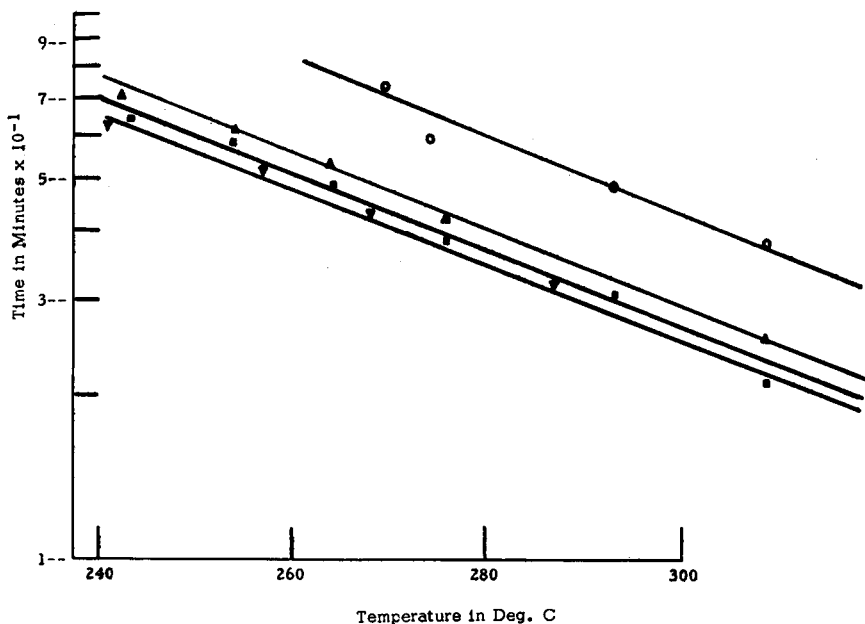

Fig. 12. Evaluation of antioxidants. Resin: (∇) Union Carbide DYNK; (□) DYNK 0.07% BR-254; (▲) DYNK 0.07% BR-3360; (O) DYNK 0.07% BR-24.
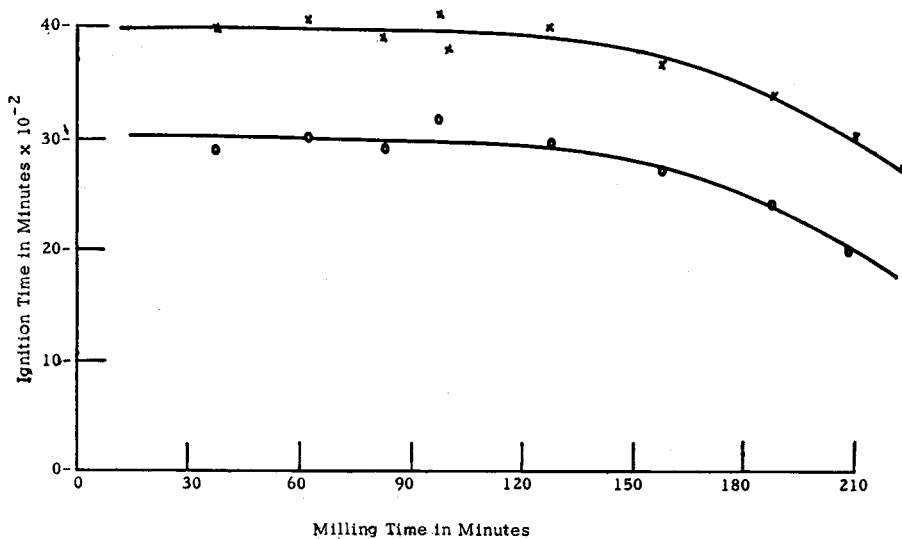

Fig. 13. Variation in ignition time with milling, Tenite 800 resin. Constant ignition temperatures: (×) 481°F.; (O) 495°F.
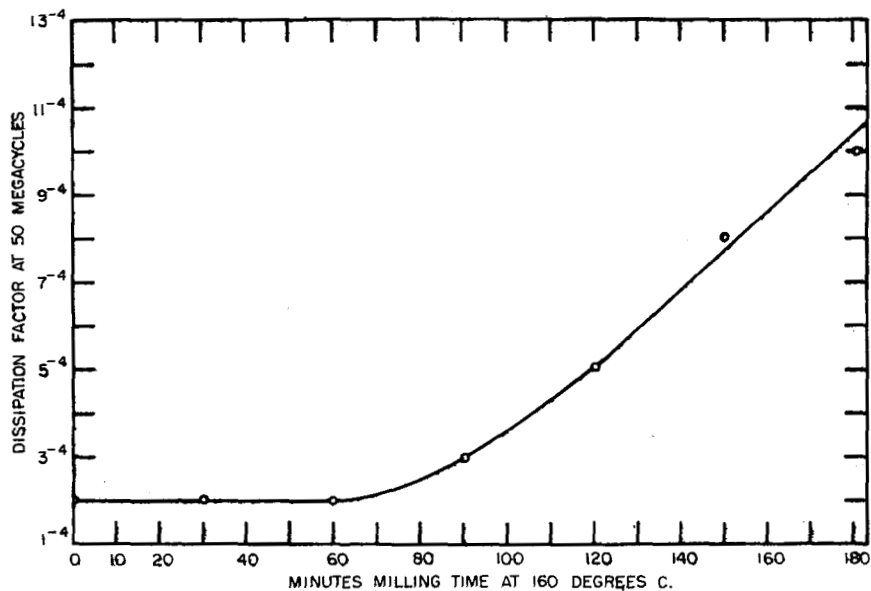
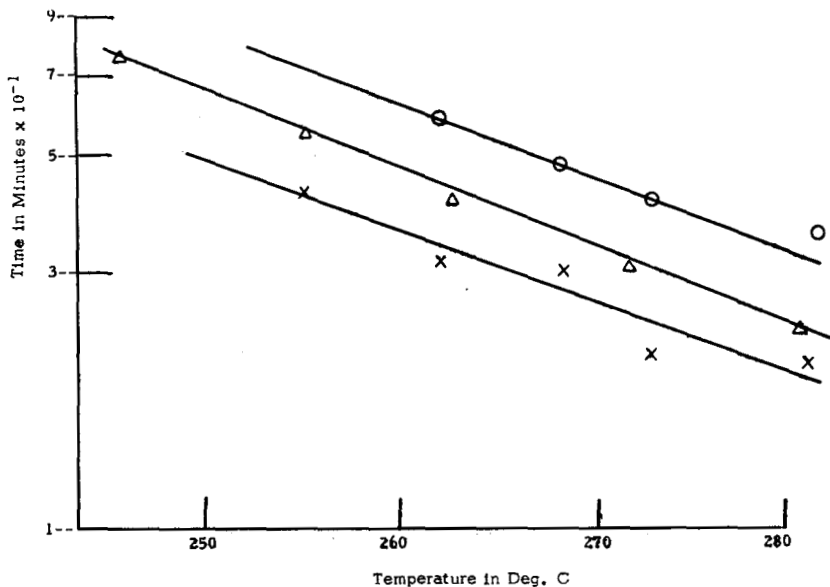Fig. 14. Dissipation factor versus milling time for Petrothene 203.

Fig. 15. Differentiation among resins with identical melt indices (M.I. 0.3): (O) Tenite series 61; (X) Tenite 810; (Δ) Alathon 3.

for precisely this purpose. Being responsive to the presence of antioxidants, it can also be used to evaluate these materials. Thus, Figure 12 depicts the results of an evaluation of three Union Carbide antioxidants by this procedure.

The ASTM procedure[13] for evaluating the oxidizability of polyethylene compositions consists of hot-mill mixing the polymer for incremental periods of time and noting when a change occurs in the electrical dissipation factor of the resin. The ignition test can serve as a substitute for the electrical measurement of the ASTM procedure. Figure 13 shows that for incrementally milled resins, plots of milling time versus ignition time, at a given ignition temperature, yield curves identical with the type that characterize dissipation factor measurements (Fig. 14) in that after a given time on the mill the ignition time of the resin undergoes progressive change.

Currently, one of the main specifications by which polyethylenes are described is that of melt index,[14] a measure of melt viscosity or of readiness to flow. Since polyethylenes of identical melt index may well differ in their oxidizability, it becomes possible to distinguish among them by the use of the lead peroxide ignition test. This is illustrated in Figure 15. As a consequence, the inclusion of a lead peroxide ignition value among the specifications for a polyethylene not only will serve as a guide to oxidizability of the polymer but will distinguish it from resins of a like melt index. Its function in this regard is as a specification adjunct to melt index values.

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Synopsis

Standardized mixtures of powdered polyethylenes and lead peroxide constitute redox systems that ignite upon the surface of a hot plate after a time interval that is

inversely related to temperature and to the oxidizability of the resin. The influence of antioxidants and of oxidation accelerators upon the lead peroxide ignition is identical with that upon the reaction of polyethylenes with oxygen gas at elevated temperatures. Methyl branching also has an identical effect on both reactions. Hence, plots of ignition time versus ignition temperature serve to characterize the oxidative reactivity of polyethylene resins. This solid–solid redox system is shown to have long shelf stability at room temperature, not to be subject to premature ignition induced by the presence of more easily oxidized contaminants, and to suffer the effect of carbon black filler by showing a more sluggish reactivity. The lead peroxide ignition test serves to distinguish among polyethylenes. It can be used to assay the antioxidative proclivities of antioxidants. It can be substituted for electrical dissipation factor measurements in following the hot mill oxidation of polyethylenes. Since this test differentiates among polyethylenes having identical melt indices, lead peroxide ignition time values can also provide a useful specification parameter in describing polyethylene resins.

Résumé

Des mélanges standards de différents polyéthylènes en poudre et de peroxyde de plomb constituent des systèmes rédox qui brulent à la surface d'une plaque chauffante après un intervalle de temps qui varie inversément à la température et qui est une fonction de l'oxydabilité de la résine. L'influence d'antioxydants et d'accélérateurs d'oxydation sur la combustion au peroxyde de plomb est identique à l'influence sur la réaction des polyéthylènes avec l'oxygène gazeux à température élevée. La ramification avec des groupements méthylés à également un effet identique sur les deux réactions. Dès lors, des graphiques du temps de combustion en fonction de la température de combustion sont utilisés à caractériser la réactivité d'oxydation des résines de polyéthylène. On démontre que ce système rédox solide–solide possède une stabilité limite à la température de chambre, qu'il n'est pas exposé à une combustion prématurée causée par la présence d'impuretés plus facilement oxydables et qu'il subit l'influence de diluants inertes puisque la réactivité s'y fait plus lentement. Le test de la combustion au peroxyde de plomb sert à faire la distinction entre les polyéthylènes. Il peut être employé pour essayer les tendances antioxydantes des antioxydants. Il peut être remplacé pour des mesures du facteur de dissipation électrique en suivant l'oxydation des polyéthylènes dans un broyeur chauffant. Puisque cet examen distingue les polyéthylènes ayant le même indice de fusion, les valeurs du temps de combustion au peroxyde de plomb peuvent donner un paramètre spécifique utile pour décrire les résines de polyéthylènes.

Zusammenfassung

Standardisierte Mischungen aus gepulvertem Polyäthylen und Bleidioxyd bilden Redoxsysteme, die sich auf einer heissen Platte nach einem Zeitintervall entzünden, das in umgekehrter Beziehung zur Temperatur steht und eine Funktion der Oxydierbarkeit des Harzes ist. Der Einfluss von Antioxydantien und von Oxydationsbeschleunigern auf die Bleidioxydentzündung is tmit dem auf die Reaktionz wischen Polyäthylen und gasförmigen Sauerstoff bei erhöhter Temperaturen identisch. Methylverzweigung hat ebenfalls auf beide Reaktionen identischen Einfluss. Auftragung der Entzündungsdauer gegen die Entzündungstemperatur kann daher zur Charakterisierung der Oxydierbarkeit von Polyäthylen dienen. Dieses Fest–Fest-Redoxsystem hat eine langdauernde Lagerungsstabilität bei Raumtemperatur, erleidet keine vorzeitige Zündung durch die Gegenwart leichter oxydierbarer Verunreinigungen und Zeigt unter dem Einfluss inerter Verdünnungsmittel eine grössere Reaktionsträgheit. Mit dem Bleidioxyd-Entzündungstest kann zwischen Polyäthylenarten unterschieden werden. Er kann bei der Verfolgung der Heissvermahlungsoxydation von Polyäthylen die Messung des elektrischen Dissipationsfaktors ersetzen. Da der Test zwischen

Polyäthylenen mit identischem Schmelzindex unterscheidet, können die Bleidioxyd-Entzündungsdauerwerte auch einen brauchbaren Parameter zur Beschreibung von Polyäthylenen liefern.