

## Induction Period in the Aging of Polypropylene\*

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### Synopsis

The ordinary methods for obtaining a rapid estimate of the useful life of a plastic, extrapolations from tests conducted at higher temperatures or at lower stabilizer concentrations than those of actual use, lead to serious errors in estimating the useful life of some stabilized polypropylene compositions. Two methods for obtaining more reliable rapid estimates of useful life have been explored and are reported here: (1) measurement of physical and chemical changes, such as weight loss, stabilizer loss, density increase, dyeability increase, and formation of carbonyl or hydroperoxide groups, which occur during the prefailure stages of oxidative deterioration at the temperature of interest (of these, measurements of stabilizer loss appear the most promising); (2) thermal development of the prefailure oxidative damage initiated at the temperature of interest. This method needs further exploration.

### Introduction

The deterioration of polypropylene and most other polymeric materials follows a course similar to that shown in Figure 1. When some property of practical importance,  $P$ , is plotted against aging time, no appreciable change in  $P$  occurs during the induction period which ends near point  $B$ . Then, easily measurable changes begin, and the plastic deteriorates with accelerating rapidity.

Under the aging conditions of interest, the time required to reach point  $B$  may be 10–20 yr., which is too long to be of practical use for the development of new formulations. The usual method for obtaining a rapid estimate of the useful life of a plastic is to carry out the aging at two or more higher temperatures and then to estimate, from the results obtained, the probable useful life at the desired temperature.<sup>1</sup> Unfortunately, the extrapolation of results obtained at higher temperatures can lead to false conclusions, as illustrated in Figure 2. If measurements had been made on the unstabilized polypropylene at temperatures  $T_1$  and  $T_2$  only, a linear extrapolation to 70°C. would have led to the conclusion that this plastic would last for 5 yr. in air at 70°C. Actually, it lasted only about 1 wk., as shown in Figure 2. Since the curve for the stabilized compositions will also be

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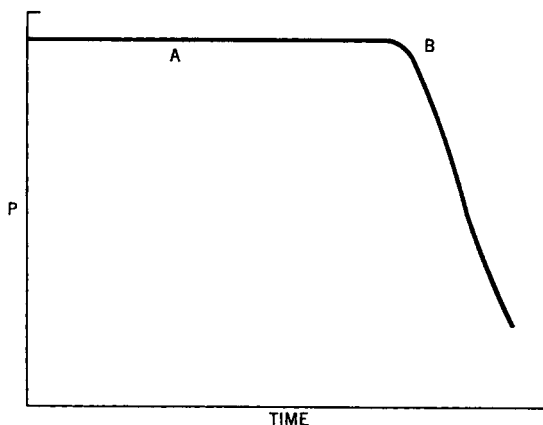


Fig. 1. Aging of polymer.

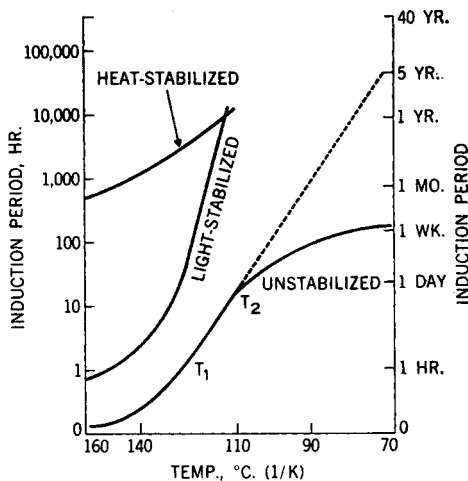


Fig. 2. Oxidative breakdown of polypropylene.

S-shaped,<sup>2</sup> a linear extrapolation of either of these curves to 70°C. would lead to an unreliable estimate.

It is of interest to note that the light-stabilized composition, containing only a 2-hydroxybenzophenone derivative, had a heat stability at 140–160°C. only slightly better than the unstabilized plastic. Yet, at 110°C. its heat stability had improved to a level better than that of the conventional heat-stabilized composition based on the usual synergistic mixture of phenolic and thio-type heat stabilizers. Hawkins and co-workers<sup>3</sup> have reported a similar comparison between a phenolic compound and carbon black as antioxidants for polyethylene, as shown in Figure 3. One of the important properties of a weathering stabilizer, such as carbon black or a derivative of 2-hydroxy-

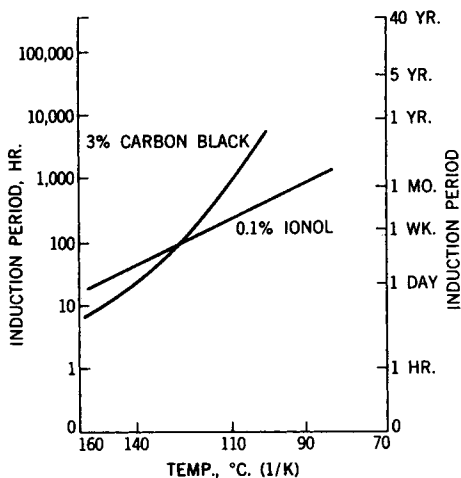


Fig. 3. Oxidative breakdown of polyethylene.<sup>3</sup>

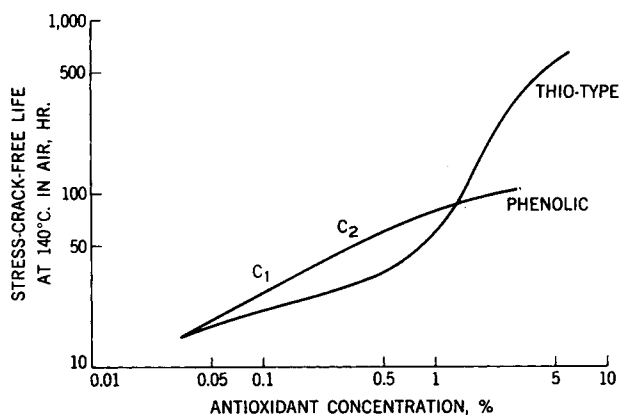


Fig. 4. Effect of antioxidant concentration on oxidative stability of polypropylene.

benzophenone, is probably its ability to function as an efficient low-temperature antioxidant.<sup>4</sup>

A second method of obtaining a rapid estimate of the useful life of a plastic is to measure the useful lifetimes of plastic formulations containing low concentrations of stabilizer and then to extrapolate the results obtained to the region of practical stabilizer concentrations. Here again, the extrapolation of results obtained at lower concentrations can lead to false conclusions, as shown in Figure 4. The useful life was taken as the time in a mechanical convection air oven at 140°C. required to crack a stressed specimen (Fig. 5). If measurements had been confined to the concentration range  $C_1$  to  $C_2$  (Fig. 4), extrapolation would have led to the conclusion that the phenolic antioxidant would perform better at the 2% concentration level than the thio-type antioxidant. However, the reverse was true.

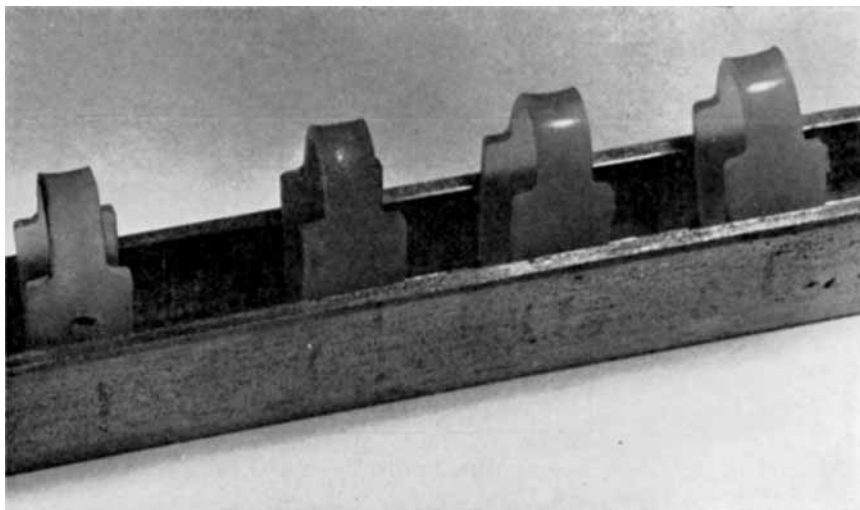


Fig. 5. Polypropylene stress-cracking specimens.

Hansen, Martin, and De Benedictis have concluded that this is not a reliable method of accelerating tests on stabilized formulations.<sup>5</sup>

A third method, perhaps more dependable than those outlined above, for obtaining a rapid estimate of the useful life of a plastic would be to age it at the actual temperature of interest to a point such as that designated by *A* in Figure 1 and then, by some sensitive measurement of the incipient aging changes which are occurring, to estimate how much longer it will take to reach a point of practical failure, such as *B*.

A fourth method of obtaining a rapid estimate of useful life is to develop the latent image of oxidative damage which must exist in the sample at point *A* of Figure 1. An example of success with this approach has been reported<sup>6</sup> as a chemical coloration test for the presence of oxidation damage on the surface of polyamide molding granules. Similarly, increases in dyeability of polyamide fibers during the early stages of oxidative deterioration have been reported.<sup>7</sup>

The purpose of this paper is to explore briefly the possible usefulness of the last two methods.

### Experimental

The following four polypropylene compositions which cover a wide range of heat stabilities were selected for testing: (1) unstabilized; (2) containing 0.3% of a typical phenolic antioxidant; (3) containing 0.5% of a typical thio-type antioxidant; (4) containing both 0.3% phenolic antioxidant and 0.5% thio-type antioxidant. These compositions were injection-molded into tensile bars  $\frac{1}{16}$  in. thick and also compression-molded into films 8 and 14 mil thick.

The useful lifetimes of these materials were determined in air at 140°C. and 110°C. Stress cracking was selected as an illustrative type of practical

failure. This stress-cracking test was carried out with the  $1/16$ -in.-thick tensile bars which were bent into a U-shape, inserted open end first into a stainless steel channel,  $5/8$  in. wide and  $1/2$  in. deep, and exposed in a mechanical convection air oven at the desired temperature until cracks became visible to the unaided eye. The time required for cracks to appear was taken as the induction period or the stress-crack-free life. Figure 5 shows the arrangement used and the appearance of cracked and uncracked specimens.

Under the third method, the following types of measurements were used in the detection of aging changes prior to the end of the induction period: (a) weight loss at 140 and 110°C. by the  $1/16$ -in.-thick tensile bars; (b) formation of carbonyl groups at 140 and 110°C. in the  $1/16$ -in.-thick tensile bars, detected by infrared absorption at  $5.82 \mu$ , both by the conventional transmission method and by a surface reflection method (attenuated total reflectance, ATR); (c) hydroperoxide formation at 125°C. in the  $1/16$ -in. tensile bars<sup>8</sup> detected by infrared absorption at  $2.9 \mu$ ; (d) loss of phenolic antioxidant at 140 and 110°C. by  $1/16$ -in.-thick tensile bars measured by ultraviolet absorption at  $280 m\mu$  (the heated bars were compression-molded to films 14 mil thick for the ultraviolet measurements); (e) increase in density of the  $1/16$ -in. tensile bars at 140 and 110°C.; (f) increase in dyeability of the 8-mil films at 140 and 110°C.; (g) electrical properties of 8-mil films.

The method for the development of the latent image of oxidative damage was aging the samples at the relatively low temperature of 110°C. for a short time to bring them to a point such as *A* in Figure 1. Then the aging was continued at the relatively high temperature of 140°C. until the sample failed (*B* in Fig. 1). Again, the stress-cracking procedure was used for these tests.

### Results and Discussion

The induction periods or stress-crack-free lifetimes of the four compositions at 140 and 110°C. are shown in Table I. At temperatures around 140°C., where heat stabilizers for polyolefins are customarily evaluated, the life of the composition which was stabilized with the synergistic combination of phenolic and thio-type antioxidants was by far the longest of the four. However, at 110°C. there was less difference between compositions 2 and 4. At a temperature where polypropylene is normally used, e.g., 70°C., it is not certain which of the compositions will last longer. Figure 6 indicates that composition 2, rather than the synergistic composition 4, might be the better of the two at 70°C.

At both 140 and 110°C., stress cracking of stabilized samples occurred at weight losses between 0.7 and 3.4% (Figs. 7 and 8). The unstabilized, stressed sample cracked at about 0.2% weight loss. Correct ranking of samples according to stability at 140°C. by measurements of weight loss was possible only after 60 hr. heating. Composition 2 remained below composition 4 in weight loss up to that time. Thus, at 140°C., as shown

TABLE I  
Oxidative Stability of Polypropylene

Composition	Observed stress-crack-free life, hr.		Decrease in 140°C. stress-crack-free life, <sup>a</sup> %	Predicted stress-crack-free life at 110°C., hr.	Time required for predicting 110°C. stress-crack-free life, hr.
	110°C.	140°C.			
1	17	2	—	—	—
2	8,930	69	2	10,000	268
3	500	24	61	328	210
4	16,900	900	3	6,700	1,073

<sup>a</sup> Caused by pre-exposure of 200 hr. at 110°C.

by Table I, very little time was saved by measuring weight loss instead of stress cracking. Likewise, at 110°C., as shown in Figure 8, weight loss by composition 2 remained below that of composition 4 until after the first 5000 hr. of heating. The weight-loss measurements offered a saving of 3930 hr. over stress-cracking measurements. It is believed that the steplike progression of weight losses observed in these compositions are real and that they reflect the existence of a series of consecutive oxidation reactions. In a recent paper,<sup>9</sup> it has been reported that when a series of polypropylene compositions containing the antioxidant copper stearate was heated in oxygen at 140°C., the weights of all samples increased for brief intervals, passing through maxima of 0.2–0.6% increase before progressively decreasing in weight.

Increases in carbonyl content of the plastic samples were measurable during the induction periods, but they did not precede the stress-cracking failures enough to serve as useful early indicators of oxidation damage. Interpretation of the measurements was complicated by loss of carbonyl-containing stabilizers.

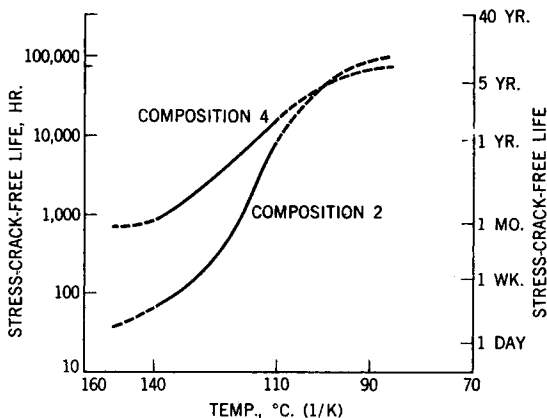


Fig. 6. Oxidative breakdown of polypropylene.

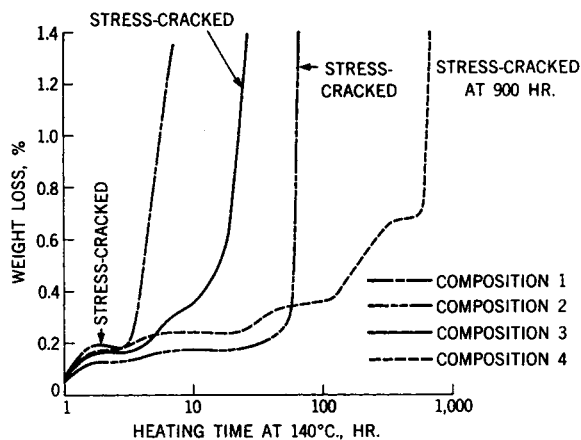


Fig. 7. Weight loss of polypropylene at 140°C.

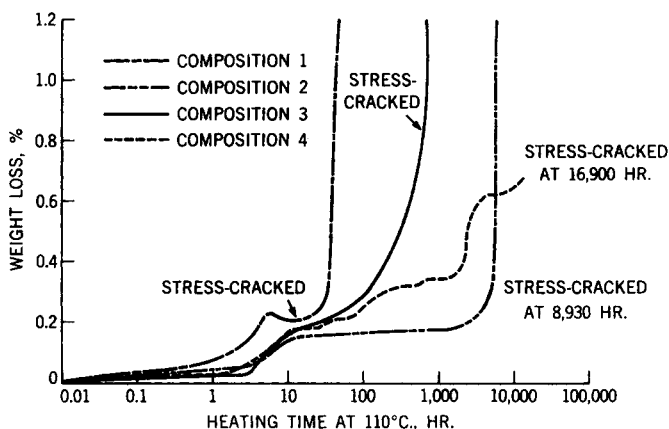


Fig. 8. Weight loss of polypropylene at 110°C.

Hydroperoxides were found only in the unstabilized composition. Even here quantitative measurements were difficult.

The densities of the specimens increased by 1–2% during the induction periods, but the measurements did not prove useful for stabilizer evaluation.

Increases in dyeability of the heated films, which were expected from oxidation of the surfaces, were observed only in the unstabilized composition.

The electrical properties, dielectric constant and dissipation factor, of the specimens did not increase measurably until stress cracking was imminent, and thus were not useful for the rapid evaluation of stabilizers.

Decreases in ultraviolet absorption by the compositions containing the phenolic antioxidant were measurable well in advance of stress-cracking failure. These decreases for compositions 2 and 4 are shown in Figure 9 as per cent phenolic antioxidant retained versus heating time. Based on

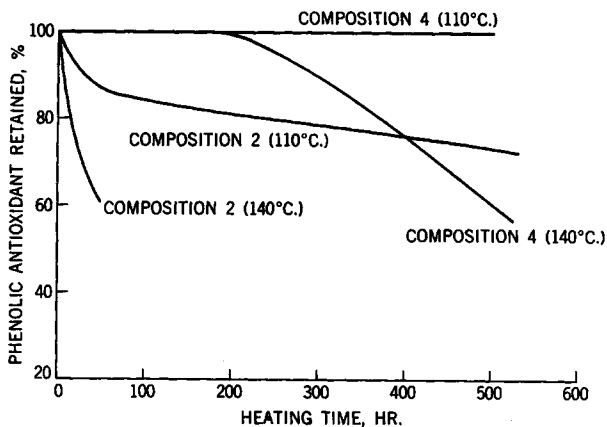


Fig. 9. Loss of phenolic antioxidant by polypropylene during heating.

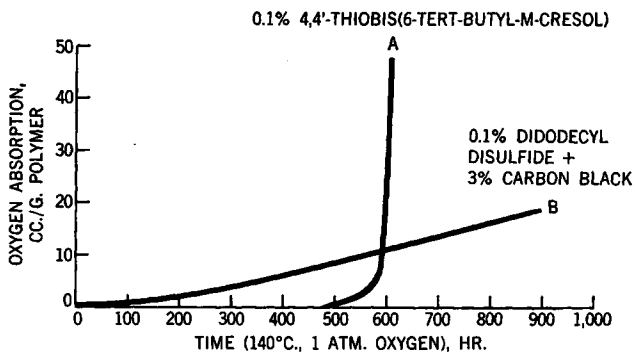


Fig. 10. Oxidation of stabilized polyethylenes.<sup>11</sup>

these data, composition 4 appeared to be superior to composition 2 after just a few hours at either 140 or 110°C.

Of the various types of measurements used in the detection of the early stages of oxidative damage, only the measurement of decreases in ultra-violet absorption by compositions containing the phenolic antioxidant seemed useful for giving early predictions of eventual failure.

The method of oxygen absorption, developed at the Bell Telephone Laboratories,<sup>10</sup> certainly permits changes to be measured during the induction period, at least for some types of stabilized polyolefin compositions. But, as shown for polyethylene in Figure 10, it is often difficult to predict ultimate failure times by oxygen absorption in the early stages of oxidation.<sup>11</sup> Up to 500 hr. at 140°C., composition A would be judged more stable than composition B. After 600 hr., however, the situation is reversed.

The results obtained from an attempt to make predictions of the useful lifetimes of stabilized polypropylenes by the latent-image-development method are shown in Table I for compositions 2, 3, and 4. The predicted



stress-crack-free life at 110°C. (column 5) was obtained by multiplying 200 hr. (the actual exposure at 110°C.) by the ratio of 100 to the per cent decrease in the 140°C. stress-crack-free life (column 4). The values in column 5 may thus be compared with the observed values for the stress-crack-free life at 110°C. (column 2). The times required to obtain estimates of the 110°C. stress-crack-free lifetimes by the latent-image-development method (column 6) may also be compared with the times required by the direct method (column 2).

Although much time-saving appears possible by use of the latent-image-development method, further work on this method is obviously needed to determine whether it will be useful in evaluating stabilized polypropylenes.

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### Résumé

Les méthodes ordinaires en vue d'obtenir une estimation rapide de la durée de vie utile d'un plastique, à savoir les extrapolations à partir d'essais effectués à des températures plus élevées et à des concentrations en stabilisant plus faibles que celles utilisées en réalité, conduisent à des erreurs importantes dans l'estimation de la durée de vie de certaines compositions stabilisées de polypropylène. On a étudié et on décrit deux méthodes pour obtenir des estimations rapides de la durée de vie plus sûres: (1) La mesure des modifications physiques et chimiques telles que la perte de poids, la perte de stabilisant, l'augmentation de groupements carbonyles ou hydroperoxydes, qui ont lieu pendant les étapes de la détérioration oxydante à la température qui présente le plus d'intérêt. Les mesures de perte de stabilisant semble être les plus intéressantes (2) L'évolution thermique de la destruction oxydante initiée à la température qui présente de l'intérêt. Cette méthode nécessite une étude plus approfondie.

### Zusammenfassung

Die gewöhnliche Methode zur raschen Gewinnung eines Wertes für die Gebrauchsdauer eines Kunststoff, nämlich eine Extrapolation aus Tests bei höherer Temperatur

oder niedrigerer Stabilisatorkonzentration, wie sie im Gebrauch angewendet werden, führt bei der Bestimmung der Gebrauchsdauer gewisser stabilisierter Polypropylenmischungen zu schwerwiegenden Irrtümern. Zwei Methoden zur raschen Gewinnung verlässlicher Werte für die Gebrauchsdauer wurden ausgearbeitet und werden hier mitgeteilt: (1) Messung physikalischer und chemischer Änderungen wie Gewichtsverlust, Stabilisatorverlust, Dichtezunahme, Anfärbbarkeitszunahme und Bildung von Carbonyl- oder Hydroperoxydgruppen, welche bei der oxydativen Schädigung bei der interessierenden Temperatur im Stadium vor dem Verlust der Gebrauchseigenschaften auftreten. Unter allen diesen scheint eine Messung des Stabilisatorverlusts am besten geeignet zu sein. (2) Thermische Entwicklung der oxydativen Schädigung vor Verlust der Gebrauchseigenschaften, initiiert bei der interessierenden Temperatur. Diese Methode muss weiter erforscht werden.

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